CHAPTER IV

RESULTS AND DISCUSSION

4.1 Purity of the Essential Amino Acids

The purity of the essential amino acids was checked by pH-metric titration and by the examination of the entire curve for deviation from the calculated shape (1).

By titrating each solution of 1.00×10^{-3} M essential amino acid in the presence of 0.10 M KCl and the constant temperature of $37.0 \pm 0.5^{o}C$, pH-values were recorded for each addition of standard solution of NaOH. The pH-metric titration data of each essential amino acid, L-isoleucine, L-leucine, L-lysine, L-methionine, L-phenylalanine, L-threonine, L-tryptophan and L-valine are shown respectively in Appendix 1A-1H. The plot of the number of moles of base added per mole ligand (a) versus pH measured (pH^{m}) gave the pH-metric titration curve of each essential amino acid as shown respectively for L-isoleucine, L-leucine, L-lysine, L-methionine, L-phenylalanine, L-threonine, L-tryptophan and L-valine by curve 1 in Figure 4.1 A - 4.1 H. The pH calculated (pH^{c}) was determined from the remaining $[H]$, $[H]$, where $[H]$ was the hydrogen-ion concentration. The $[H]_r$ was obtained from the relationship; $[H]_r = [H]_s - [OH]_a$ where the $[H]_s$ was the $[H]$ in the solution and the $[OH]_a$ was the hydroxide-ion concentration in the solution that calculated from the concentration of the standard NaOH solution added. The $[H]_s$ was given by equation (2.1).

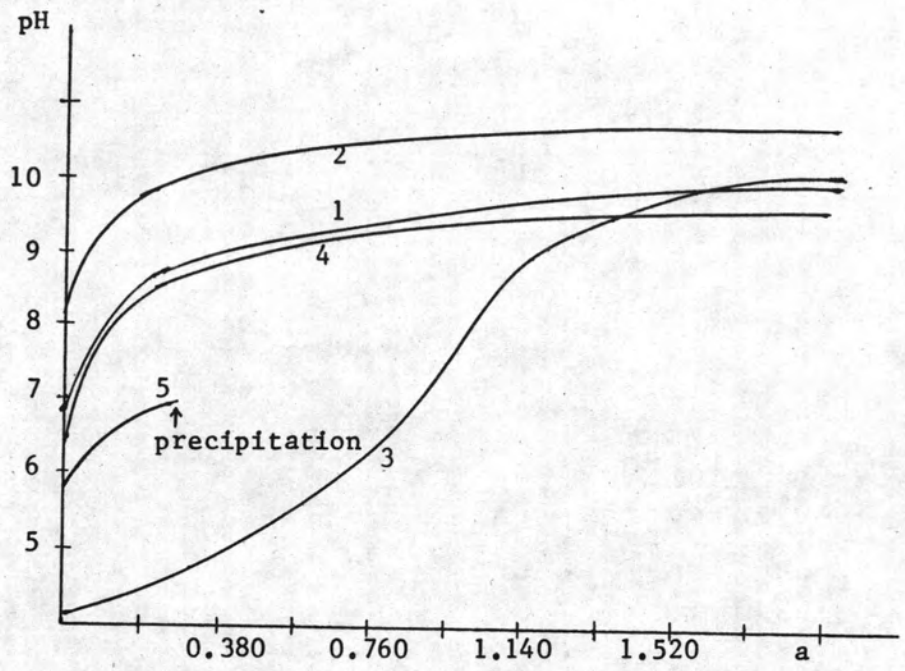

Figure 4.1 A pH-metric titration curve of 1.00×10^{-3} M L-isoleucine and 5.00×10^{-4} M metal ion ;

1. L-isoleucine only;
2. L-isoleucine only (calculated curve),
3. L-isoleucine + Cd(II) ion,
4. L-isoleucine + Mn(II) ion and
5. L-isoleucine + Pb(II) ion

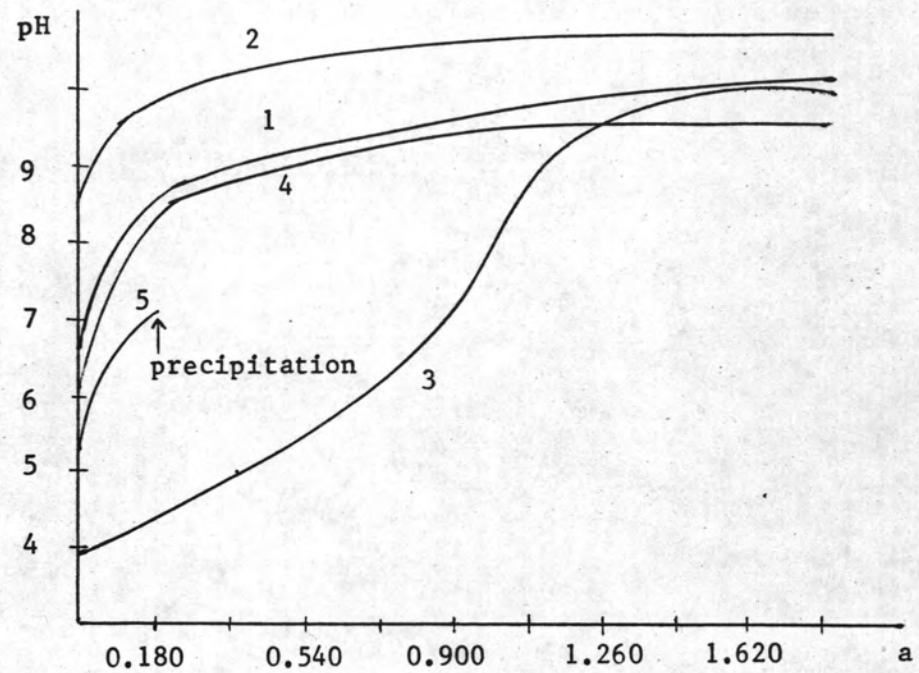

Figure 4.1 B pH-metric titration curve of 1.00×10^{-3}M L-leucine and 5.00×10^{-4}M metal ion;

1. L-leucine only,
2. L-leucine only (calculated curve),
3. L-leucine + Cd(II) ion,
4. L-leucine + Mn(II) ion and
5. L-leucine + Pb(II) ion

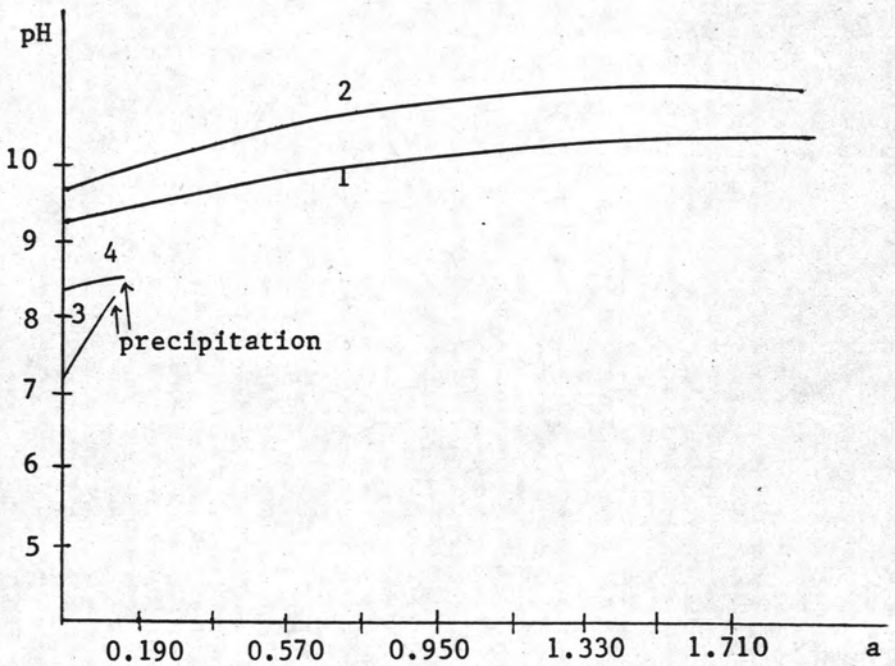

Figure 4.1 C pH-metric titration curve of 1.00×10^{-3}M L-lysine and 5.00×10^{-4}M metal ion;

1. L-lysine only,
2. L-lysine only (calculated curve),
3. L-lysine + Cd(II) ion,
4. L-lysine + Mn(II) ion and precipitation for L-lysine + Pb(II) ion

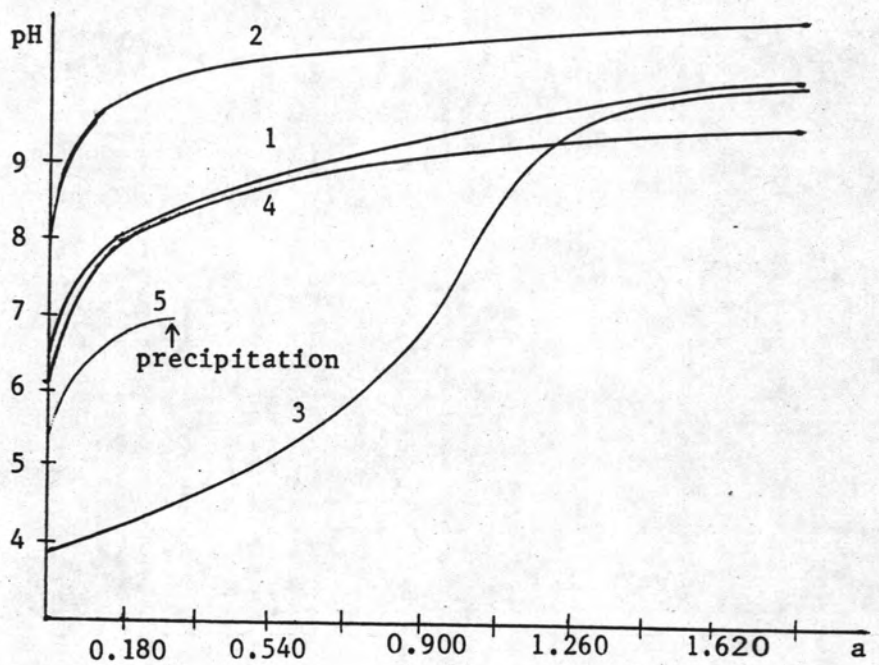

Figure 4.1 D pH-metric titration curve of 1.00×10^{-3}M L-methionine and 5.00×10^{-4}M metal ion ;

1. L-methionine only,
2. L-methionine only (calculated curve),
3. L-methionine + Cd(II) ion,
4. L-methionine + Mn(II) ion and
5. L-methionine + Pb(II) ion

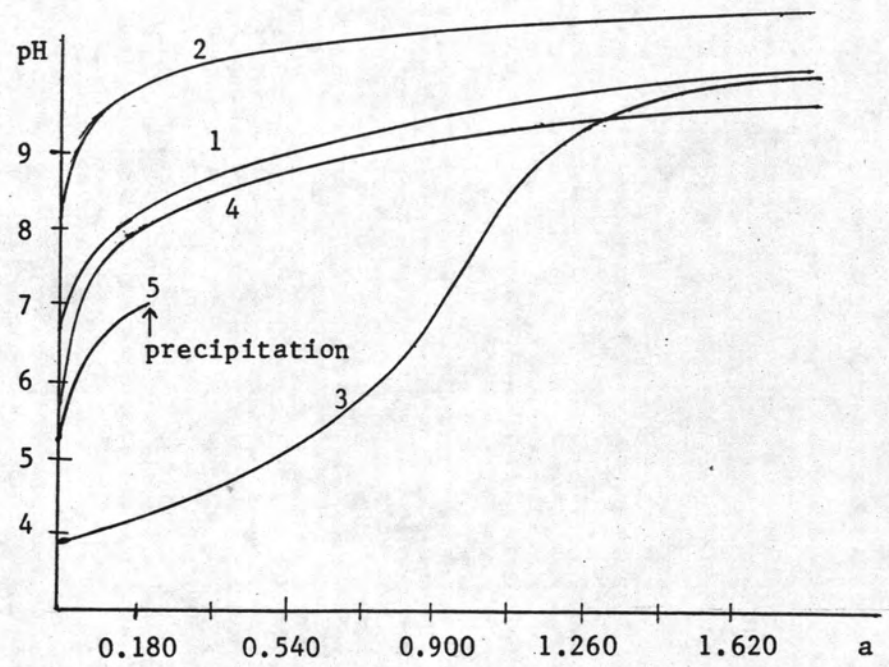

Figure 4.1 E pH-metric titration curve of 1.00×10^{-3}M L-phenylalanine and 5.00×10^{-4}M metal ion ;

1. L-phenylalanine only,
2. L-phenylalanine only (calculated curve),
3. L-phenylalanine + Cd(II) ion,
4. L-phenylalanine + Mn(II) ion and
5. L-phenylalanine + Pb(II) ion

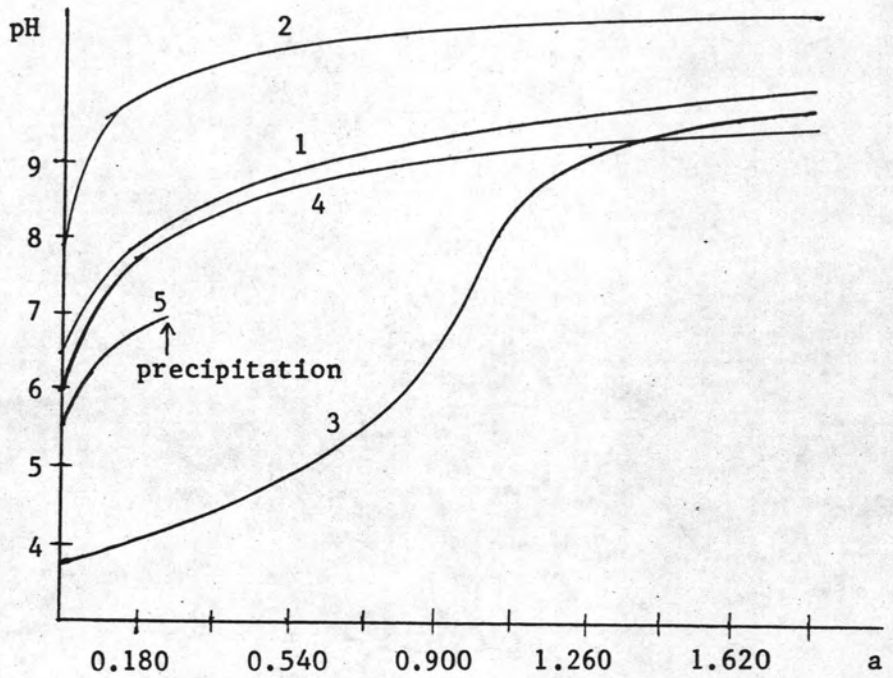

Table 4.1 F pH-metric titration curve of 1.00×10^{-3} M L-threonine and 5.00×10^{-4} M metal ion;

1. L-threonine only,
2. L-threonine only (calculated curve),
3. L-threonine + Cd(II) ion,
4. L-threonine + Mn(II) ion and
5. L-threonine + Pb(II) ion

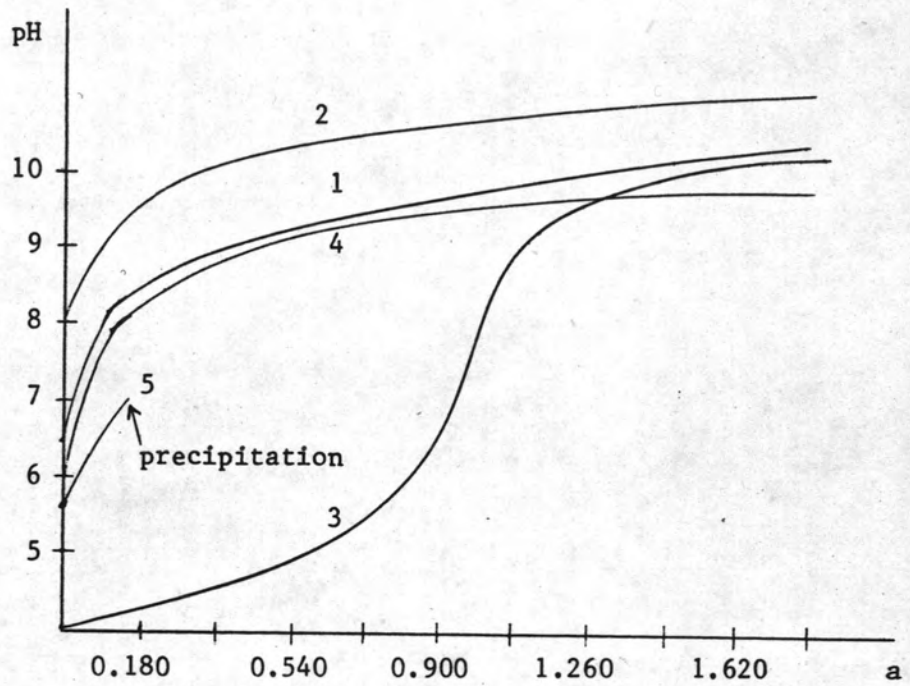

Figure 4.1G pH-metric titration curve of 1.00×10^{-3} M L-tryptophan and 5.00×10^{-4} M metal ion;

1. L-tryptophan only,
2. L-tryptophan only (calculated curve),
3. L-tryptophan + Cd(II) ion,
4. L-tryptophan + Mn(II) ion and
5. L-tryptophan + Pb(II) ion

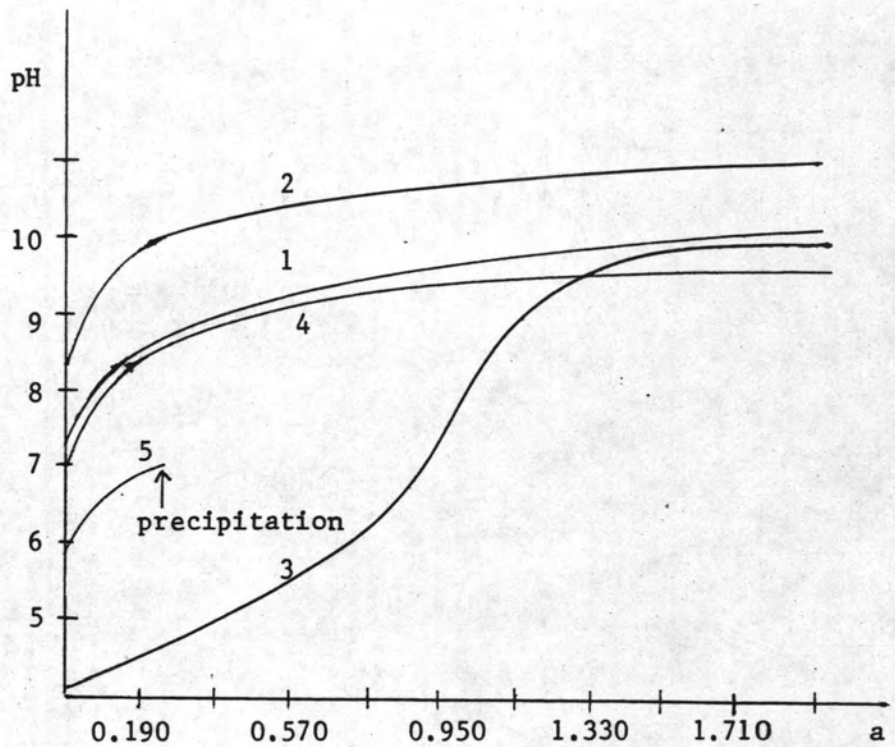

Figure 4.1 H pH-metric titration curve of 1.00×10^{-3}M L-valine and 5.00×10^{-4}M metal ion;

1. L-valine only,
2. L-valine only (calculated curve),
3. L-valine + Cd(II) ion,
4. L-valine + Mn(II) ion and
5. L-valine +Pb(II) ion

The plot of "a" versus pH^c gave the calculated curve of each essential amino acid (see curve 2 in Figure 4.1 A - 4.1 H). No deviation of the calculated curve from the titration curve of all essential amino acids as seen by curve 1 and 2 in Figure 4.1 A - 4.1 H was shown, thus, the purity of the analar grade of all essential amino acids was satisfied for this study.

4.2 The Acid-Dissociation Constants (K_a) of the Essential Amino Acids

The K_a-values of the essential amino acids were studied by pH-metric titration technique under the pressent experimental conditions, the constant ionic strength of 0.10 M KCl and the constant temperature of 37.0 ± 0.5°C

From the pH-metric titration curve of each essential amino acid (curve 1 in Figure 4.1 A - 4.1 H), many equidistant points in the buffer region on each curve were chosen at various values of "a" to calculate the corresponding value of $\{T_L-(aT_L + [H] - [OH])\}$ and $\{[H](aT_L + [H]-[OH])\}$ of each essential amino acid. $[H]$ was obtained from the pH-reading by the relationship; $[H] = 10^{-pH}$. $[OH]$ was calculated from the relationship; $[H][OH] = 10^{-pK_w}$ where pK_w at 37°C was taken from Childs and Perrin (6) to be 13.622. T_L, the total concentration of ligand, was obtained directly from the experimental conditions to be 1.00×10^{-3} M. The calculated corresponding values of $\{T_L-(aT_L + [H] - [OH])\}$ and $\{[H](aT_L + [H] - [OH])\}$ at various values of "a" from pH-metric titration curve of each essential amino acid are shown respectively in Table 4.1 A - 4.1 H. Fitting the values of $\{T_L-(aT_L + [H] - [OH])\}$ and $\{[H](aT_L + [H] - [OH])\}$ by least squares treatment, the resulting linearity that passed through the origin was obtained for every essential amino acid studied. These

Table 4.1 A Calculated values of $\{T_L-(aT_L+[H]-[OH])\}$ and $\{[H](aT_L+[H]-[OH]\}$ at various values of "a" from pH-metric titration curve of L-isoleucine

a	$\{T_L-(aT_L+[H]-[OH])$ x 10^4	$\{[H](aT_L+[H]-[OH]\}$x 10^{13}
0.190	8.024	4.901
0.285	7.080	4.362
0.380	6.172	3.775
0.475	5.292	3.361
0.570	4.443	3.007
0.665	3.618	2.741

Table 4.1 B Calculated values of $\{T_L-(aT_L+[H]-[OH])\}$ and $\{[H](aT_L+[H]-[OH]\}$ at various values of "a" from pH-metric titration curve of L-leucine

a	$\{T_L-(aT_L+[H]-[OH])\}$ x 10^4	$\{[H](aT_L+[H]-[OH]\}$x10^3
0.180	8.116	4.758
0.270	7.222	4.032
0.360	6.361	3.487
0.450	5.533	3.027
0.540	4.731	2.706
0.630	3.953	2.465

Table 4.1 C Calculated values of $\{T_L - (aT_L+[H]-[OH]\}$ and $\{[H](aT_L+[H]-[OH]\}$ at various values of "a" from pH-metric titration curve of L-lysine

a	$\{T_L-(aT_L+[H]-[OH]\}x10^4$	$\{[H](aT_L+[H]-[OH]\}x10^{13}$
0.380	7.021	16.843
0.475	6.303	15.121
0.570	5.624	13.491
0.665	4.930	12.304
0.760	4.289	9.888
0.855	3.703	9.043
0.950	3.117	8.073

Table 4.1 D Calculated values of $\{T_L-(aT_L+[H]-[OH]\}$ and $\{[H](aT_L+[H]-[OH]\}$ at various values of "a" from pH-metric titration curve of L-methionine

a	$\{T_L-(aT_L+[H]-[OH]\}x10^4$	$\{[H](aT_L+[H]-[OH]\}x10^{13}$
0.180	8.065	14.133
0.270	7.133	12.046
0.360	6.226	10.235
0.450	5.342	8.941
0.540	4.488	7.486
0.630	3.655	6.534

Table 4.1 E Calculated values of $\{T_L-(aT_L+[H]-[OH]\}$ and $\{[H](aT_L+[H]-[OH]\}$ at various values of "a" from pH-metric titration curve of L-phenylalanine

a	$\{T_L-(aT_L+[H]-[OH]\}x10^4$	$\{[H](aT_L+[H]-[OH]\}$ x 10^{13}
0.180	8.086	11.611
0.270	7.165	10.126
0.360	6.266	9.014
0.450	5.393	7.872
0.540	4.551	6.586
0.630	3.742	5.476
0.720	2.975	4.449

Table 4.1 F Calculated values of $\{T_L-(aT_L+[H]-[OH]\}$ and $\{[H](aT_L+[H]-[OH]\}$ at various values of "a" from pH-metric titration curve of L-threonine

a	$\{T_L-(aT_L+[H]-[OH]\}x10^4$	$\{[H](aT_L+[H]-[OH]\}x\ 10^{13}$
0.180	8.058	18.276
0.270	7.121	25.955
0.360	6.202	14.900
0.450	5.311	12.433
0.540	4.444	10.425
0.630	3.601	8.898

Table 4.1 G Calculated values of $\{T_L-(aT_L+[H]-[OH]\}$ and $\{[H](aT_L+[H]-[OH]\}$ at various values of "a" from pH-metric titration curve of L-tryptophan

a	$\{T_L-(aT_L+[H]-[OH]\}\times 10^4$	$\{[H](aT_L+[H]-[OH]\} \times 10^{13}$
0.180	8.115	4.544
0.270	7.219	3.945
0.360	6.352	3.496
0.450	5.537	2.888
0.540	4.728	2.646
0.630	3.989	2.233
0.720	3.301	1.884
0.810	2.619	1.685
0.900	2.076	1.368

Table 4.1 H Calculated values of $\{T_L-(aT_L+[H]-[OH]\}$ and $\{[H](aT_L+[H]-[OH]\}$ at various values of "a" from pH-metric titration curve of L-valine

a	$\{T_L-(aT_L+[H]-[OH]\}\times 10^4$	$\{[H](aT_L+[H]-[OH]\} \times 10^{13}$
0.190	8.013	5.663
0.285	7.059	5.166
0.380	6.1 4	4.370
0.475	5.242	4.089
0.570	4.392	3.488
0.665	3.596	2.882

linear plots of each essential amino acid are shown respectively in Figure 4.2 A - 4.2 H. By equation (2.5), Ka-value of each essential amino acid was obtained from the slope of its linearity. The values of the linear correlation coefficient (γ) of each linearity of each essential amino acid including Ka and pKa of all essential amino acids were collected as shwon in Table 4.2. These Ka-values were used throughout in this present work.

4.3 Complex Formation by pH-metric Titration Technique

The complex formation of interesting metal ions, Cd(II), Mn(II) and Pb(II) ion, with those essential amino acids was determined first by pH-metric titration technique. The experimental conditions used were the same as those of essential amino acids, the constant ionic strength of 0.10 M KCl and the constant temperature of $37.0 \pm 0.5^{\circ}C$.

4.3.1 Cd(II)-Essential Amino Acid Systems

After adding the solution of 5.00×10^{-4} M Cd(II) ion into the solution of 1.00×10^{-3} M essential amino acid, no physical change was observed and the mixture still colorless for all systems. By titrating each solution of 1.00×10^{-3} M essential amino acid in the presence of 5.00×10^{-4} M Cd(II) ion with standard NaOH solution at the same experimental conditions mentioned above, pH-values were recorded for each addition of standard NaOH solution. The pH-metric titration data are listed respectively for the systems of Cd(II)-L-isoleucine, Cd(II)-L-leucine, Cd(II)-L-lysine, Cd(II)-L-methionine, Cd(II)-L-phenylalanine, Cd(II)-L-threonine, Cd(II)-L-tryptophan and

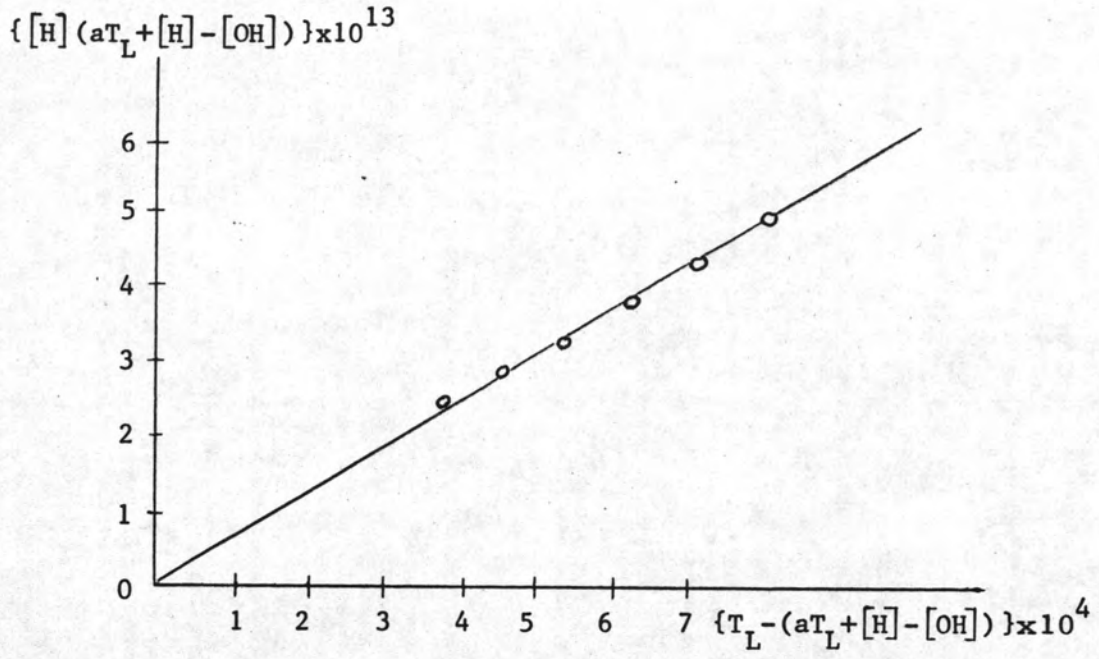

Figure 4.2 A The relationship between $\{T_L-(aT_L+[H]-[OH])\}$ and $\{[H](aT_L+[H]-[OH])\}$ of L-isoleucine

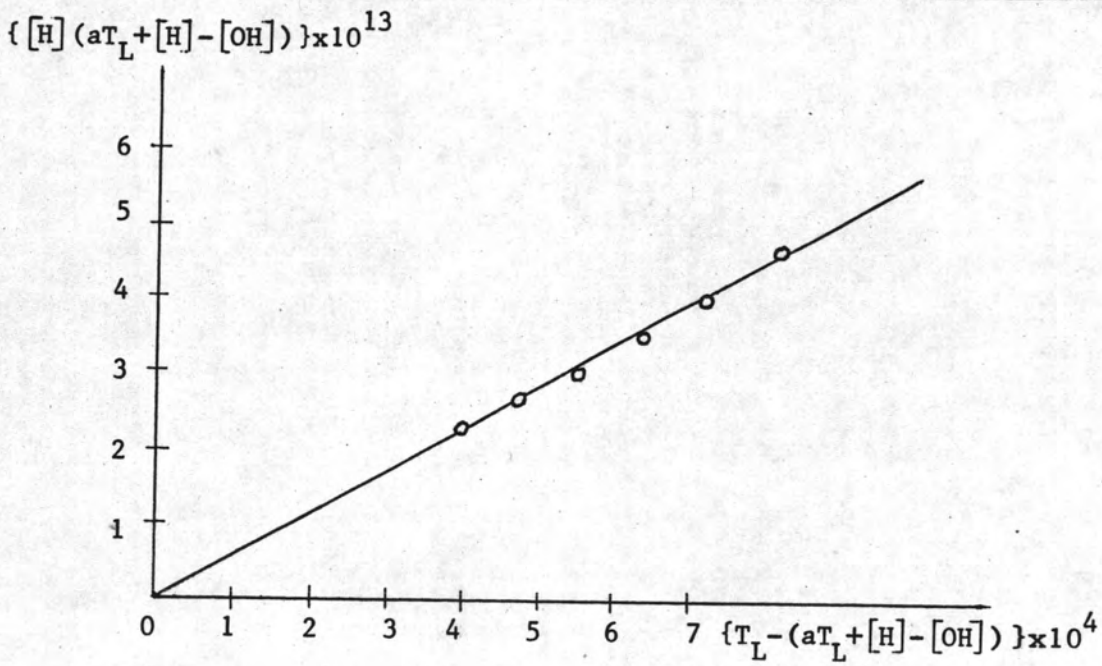

Figure 4.2 B The relationship between $\{T_L-(aT_L+[H]-[OH])\}$ and $\{[H](aT_L+[H]-[OH])\}$ of L-leucine

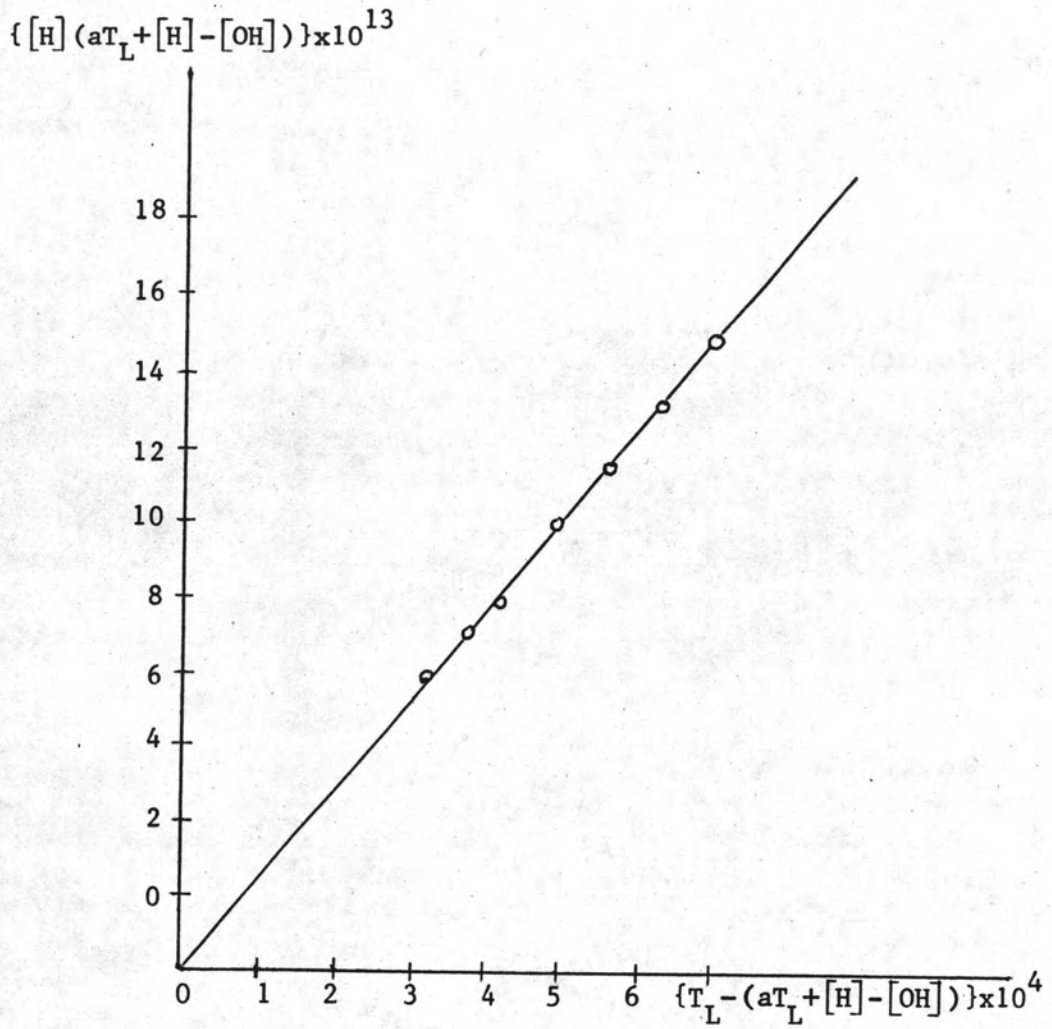

Figure 4.2 C The relationship between $\{T_L-(aT_L+[H]-[OH])\}$ and $\{[H](aT_L+[H]-[OH])\}$ of L-lysine

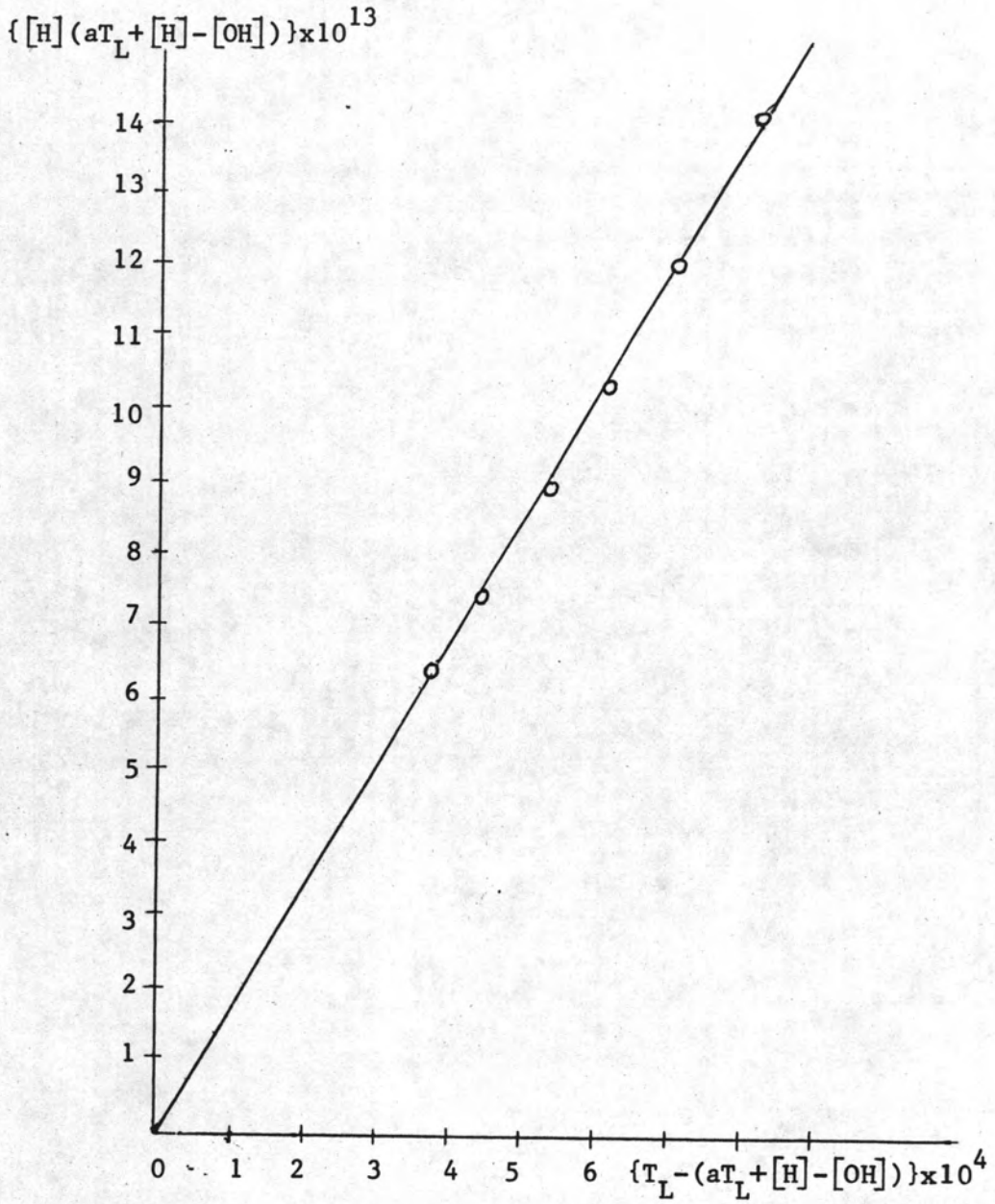

Figure 4.2 D The relationship between $\{T_L-(aT_L+[H]-[OH])\}$ and $\{[H](aT_L+[H]-[OH])\}$ of L-methionine

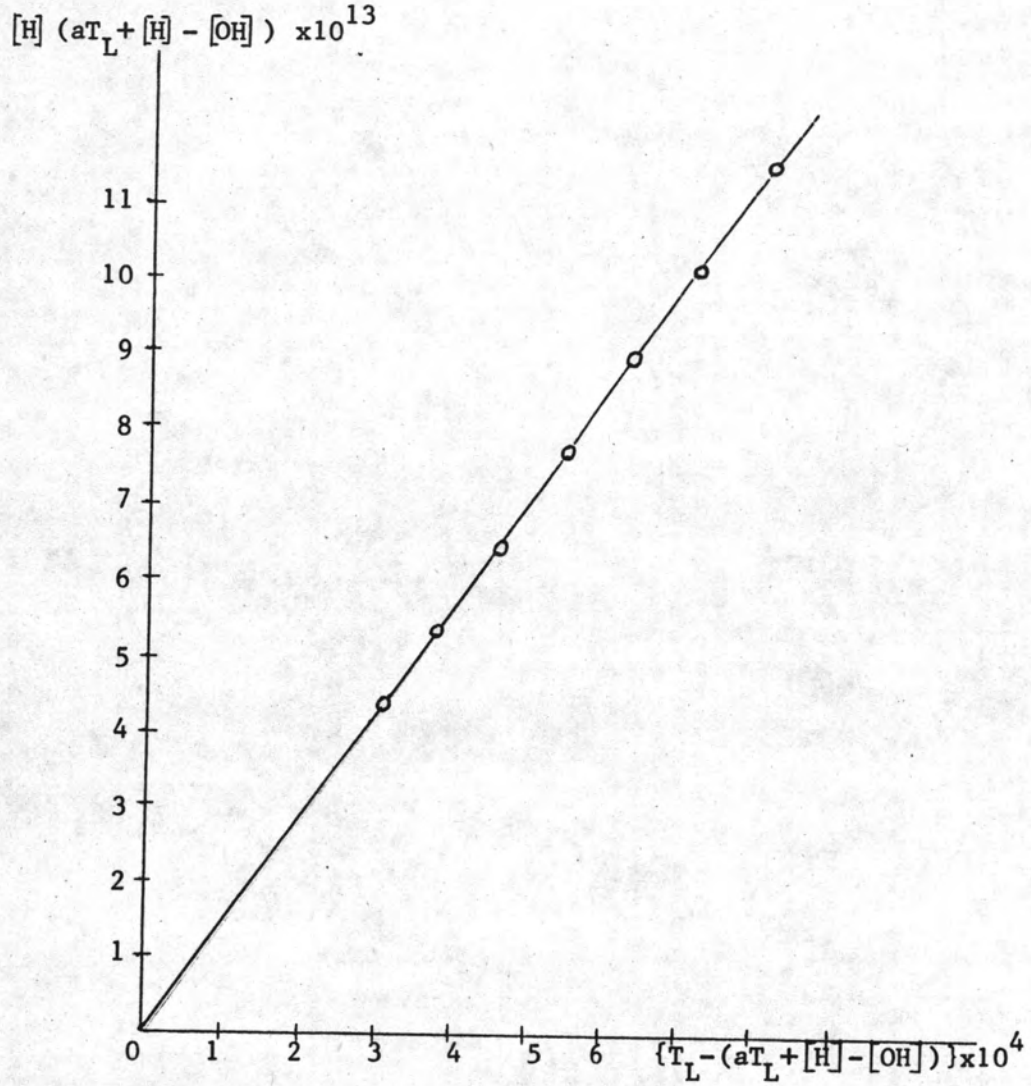

Figure 4.2 E The relationship between $\{T_L-(aT_L+[H]-[OH])\}$ and $\{[H](aT_L+[H]-[OH])\}$ of L-phenylalanine

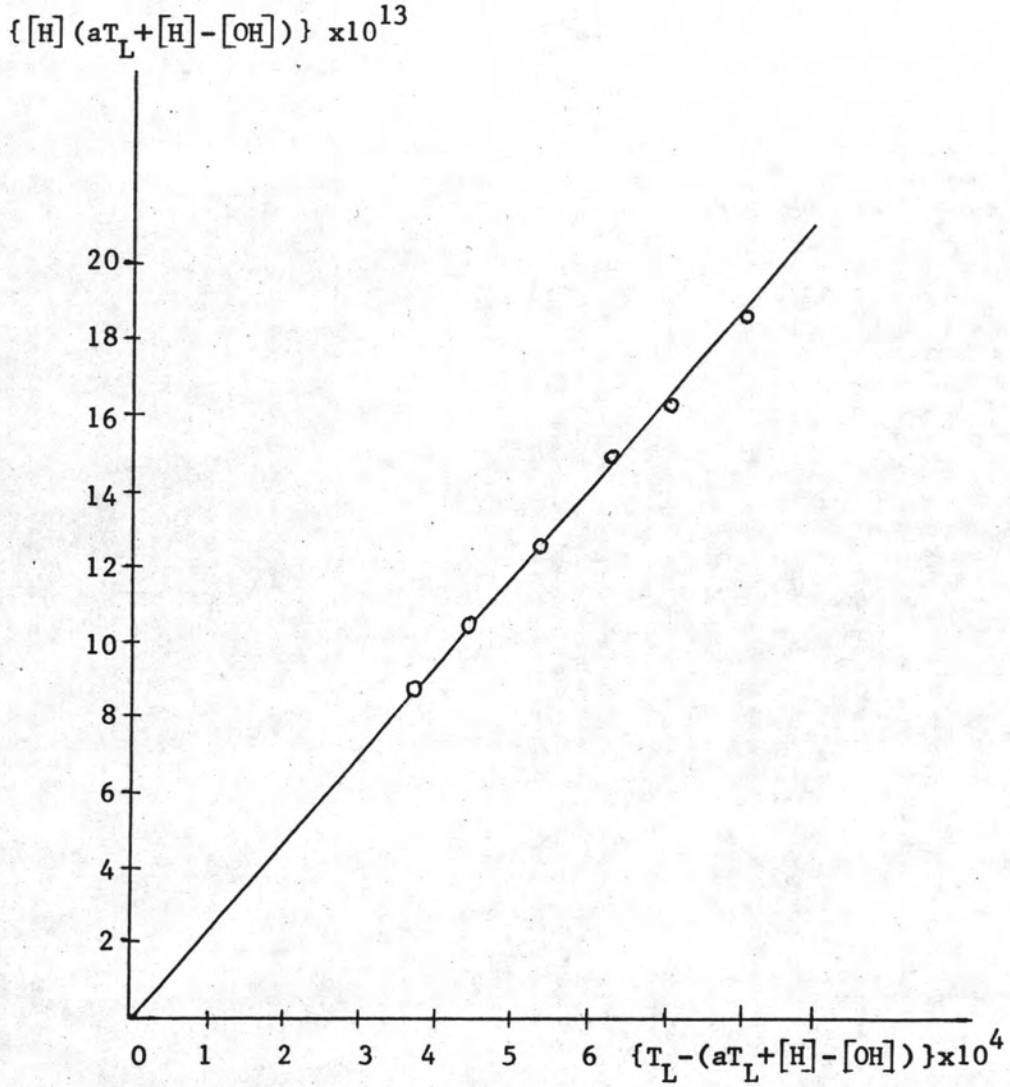

Figure 4.2 F The relationship between $\{T_L-(aT_L+[H]-[OH])\}$ and $\{[H](aT_L+[H]-[OH])\}$ of L-threonine

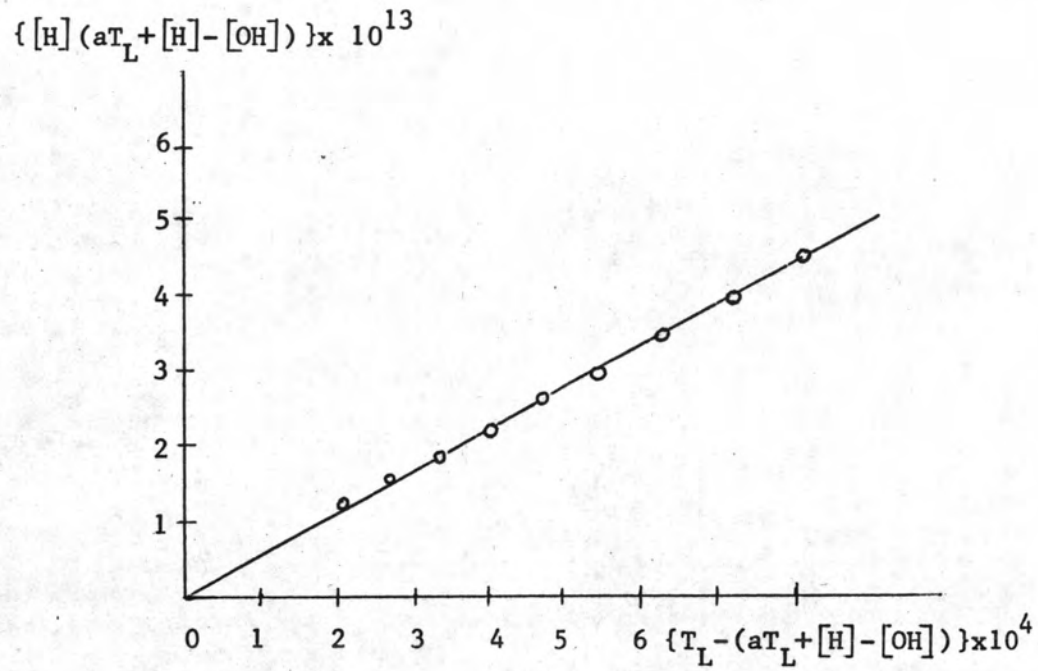

Figure 4.2 G The relationship between $\{T_L-(aT_L+[H]-[OH])\}$ and $\{[H](aT_L+[H]-[OH])\}$ of L-tryptophan

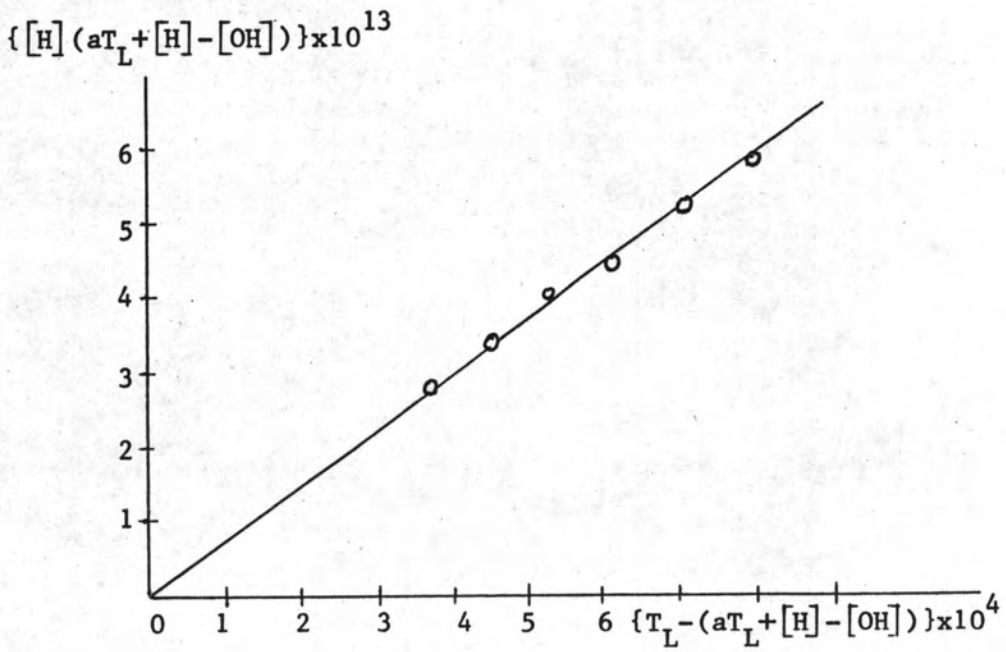

Figure 4.2 H The relationship between $\{T_L-(aT_L+[H]-[OH])\}$ and $\{[H](aT_L+[H]-[OH])\}$ of L-valine

Table 4.2 Obtained values from linear relation between $T_L-(aT_L+[H]-[OH]$ and $\{[H](aT_L+[H]-[OH])\}$ of the essential amino acids by pH-metric titration technique

Essential Amino Acid	linear Correlation Coefficient (γ)	Acid-dissociation Constant	
		Ka	pKa
L-isoleucine	0.998	5.722×10^{-10}	9.242
L-leucine	0.987	5.485×10^{-10}	9.261
L-lysine	0.996	2.310×10^{-9}	8.636
L-methionine	0.995	1.719×10^{-9}	8.765
L-phenylalanine	0.999	1.390×10^{-9}	8.857
L-threonine	0.996	2.112×10^{-9}	8.675
L-tryptophan	0.950	6.338×10^{-10}	9.198
L-valine	0.984	7.158×10^{-10}	9.145

Cd(II)-L-valine in Appendix 2A-2H. The precipitate occurred during the titration of the Cd(II)-L-lysine system at pH 8.15 (see Appendix 2C) and the pH-metric titration of this system could not be performed further because of the interference of the precipitate that resulted in the fluctuation of pH-readings. The number of moles of base added per mole ligand (a) were calculated as in the preceding section. The plot of "a" versus resulting pH gave the pH-metric titration curve of each Cd(II)-essential amino acid system (see curve 3 in Figure 4.1 A - 4.1 H). The resulting pH-metric titration curves of all systems (excepted of Cd(II)-L-lysine system) showed a clear inflection at a = 1 which meant that one proton was displaced from the essential amino acid. This evidence indicated that the formation of the complexes was taken place in the systems of Cd(II)-L-isoleucine, Cd(II)-L-leucine, Cd(II)-L-methionine, Cd(II)-L-phenylalanine, Cd(II)-L-threonine, Cd(II)-L-tryptophan, Cd(II)-L-valine and the precipitation was taken place in the system of Cd(II)-L-lysine. Many sequential points on each pH-metric titration curve of Cd(II)-essential amino acid systems as shwon in Figure 4.1 A - 4.1 H, excepted on Cd(II)-L-lysine system as seen in Figure 4.1 C, were selected at various values of "a" to calculated the corresponding values of $[L]$ by equation (2.15), $\frac{T_M - [L]X}{[L]^2 X}$ and $\frac{T_L - [L]X}{[L]^3 X}$. The values of a, $[L]$, $\frac{T_M - [L]X}{[L]^2 X}$ and $\frac{T_L - [L]X}{[L]^3 X}$ of the systems of Cd(II)-L-isoleucine, Cd(II)-L-leucine, Cd(II)-L-methionine, Cd(II)-L-phenylalanine, Cd(II)-L-threonine, Cd(II)-L-tryptophan and Cd(II)-L-valine were shown

respectively in Table 4.3 A - 4.3 G. Fitting the values of $\frac{T_L - [L]X}{[L]^3X}$ and $\frac{T_M - [L]X}{[L]^2X}$ by least squares treatment, the resulting linearity was obtained for all systems. These linear plots of all systems are shown respectively in Figure 4.3 A - 4.3 G. By equation (2.18), K_1 of each Cd(II)-essential amino acid complex can be determined from the slope and K_2 from the intercept of its linearity. The acceptable values of the slope were negative that made the K_1 positive (slope $=-1/K_1$) and of the intercept were positive (intercept $= K_2$). The negative slope and the positive intercept were all found from the linearity of Cd(II)-essential amino acid complexes (see Figure 4.3 A - 4.3 G). So, the values of the stepwise stability constants, K_1 and K_2, were provided for the complexes of Cd(II) ion with L-isoleucine, Cd(II) ion with L-leucine, Cd(II) ion with L-methionine, Cd(II) ion with L-phenylalanine, Cd(II) ion with L-threonine, Cd(II) ion with L-tryptophan and Cd(II) ion with L-valine. From the obtained values of the stepwise stability constants, K_1 and K_2, and the structure of the essential amino acids, it can be said that the composition of the 1:2 complexes of Cd(II) ion to L-isoleucine, Cd(II) ion to L-leucine, Cd(II) ion L-methionine, Cd(II) ion to L-phenylalanine, Cd(II) ion to L-threonine, Cd(II) ion to L-tryptophan and Cd(II) ion to L-valine was probably indicated in the solution and these complexes occurred in stepwise manner from the 1:1 complexes. The values of the linear correlation coefficient (γ) for each linearity of Cd(II)-essential amino acid complexes including K_1, log K_1, K_2 and log K_2 of their complexes are list in Table 4.4.

Table 4.3 A Calculated values of L , $\frac{T_M-[L]X}{[L]^2X}$ and $\frac{T_L-[L]X}{[L]^3X}$ at various values of "a" from pH-metric titration curve of Cd(II) -L-isoleucine system

a	[L]		$\frac{T_M-[L]X}{[L]^2X}$		$\frac{T_L-[L]X}{[L]^3X}$	
0.114	9.65	$\times10^{-9}$	-4.16		2.11	
0.152	1.09		-3.49		2.01	
0.190	1.28		-2.76	$\times10^{7}$	1.79	$\times10^{15}$
0.228	1.54		-2.12		1.47	
0.266	1.81		-1.64		1.24	
0.304	2.21		-1.18		9.77	
0.343	2.70	$\times10^{-8}$	-8.30		7.57	
0.381	3.27		-5.44		6.02	
0.419	4.14		-3.08	$\times10^{6}$	4.35	
0.457	4.86		-1.40		3.66	$\times10^{14}$
0.495	6.09		-6.48	$\times10^{3}$	2.69	
0.533	7.76		1.01		1.92	
0.571	9.60		1.79		1.46	
0.609	1.20		2.41		1.10	
0.647	1.57		2.66		7.45	
0.685	1.84		3.20	$\times10^{6}$	6.44	
0.723	2.27	$\times10^{-7}$	3.58		5.09	
0.761	3.17		3.46		3.18	
0.799	3.66		4.08		2.98	$\times10^{13}$
0.838	4.91		4.22		2.13	
0.876	6.52		4.59		1.64	
0.894	7.51		6.28		1.85	

Table 4.3 B Calculated values of $[L]$ $\frac{T_M-[L]X}{[L]^2X}$ and $\frac{T_L-[L]X}{[L]^3X}$ at vacious values of "a" from pH-metric titration curve of Cd (II) -L-leucine system

a	$[L]$		$\frac{T_M-[L]X}{[L]^2X}$		$\frac{T_L-[L]X}{[L]^3X}$	
0.253	1.36		-2.26		2.12	
0.289	1.63		-1.67	$\times 10^{7}$	1.72	$\times 10^{15}$
0.325	1.36		-1 27		1.53	
0.362	2.33		-8.53		1.11	
0.398	2.70		-5.65	$\times 10^{6}$	9.53	
0.434	3.43	$\times 10^{-8}$	-3.02		6.74	
0.470	4.42		-9.84		4.67	$\times 10^{14}$
0.506	5.43		4.13	$\times 10^{5}$	3.54	
0.542	6.62		1.53		2.74	
0.579	8.39		2.32		1.97	
0.615	1.03		2.99		1.52	
0.651	1.29		3.38		1.12	
0.687	1.59		3.79		8.72	
0.723	1.93		4.22	$\times 10^{6}$	7.06	
0.759	2.42	$\times 10^{-7}$	4.48		5.41	
0.796	3.04		4.75		4.20	$\times 10^{13}$
0.832	3.82		5.09		3.31	
0.868	4.68		5.92		2.99	
0.904	6.46		6.45		2.24	

Table 4.3 C Calculated values of $[L]$, $\frac{T_M-[L]X}{[L]^2X}$ and $\frac{T_L-[L]X}{[L]^3X}$ at various values of "a" from pH-metric titration curve of Cd(II) -L-methionine system

a	$[L]$		$\frac{T_M-[L]X}{[L]^2X}$		$\frac{T_L-[L]X}{[L]^3X}$	
0.036	1.26		-3.24		1.16	
0.072	1.49		-2.80		1.05	$\times 10^{15}$
0.108	1.57		-2.41		9.83	
0.144	1.83		-1.98	$\times 10^{7}$	8.25	
0.180	1.97		-1.71		8.38	
0.216	2.28		-1.38		7.14	
0.252	2.76		-1.05		5.52	
0.288	3.17	$\times 10^{-8}$	-8.19		4.79	$\times 10^{14}$
0.325	3.71		-6.05		4.00	
0.361	4.44		-4.22	$\times 10^{6}$	3.17	
0.397	5.16		-2.77		2.68	
0.433	6.41		-1.47		1.98	
0.469	7.74		-4.83		1.54	
0.505	9.52		2.92	$\times 10^{5}$	1.16	
0.541	1.14		8.90		9.26	
0.577	1.41		1.39		7.01	
0.613	1.66		1.83		5.84	
0.649	2.07		2.12		4.38	
0.685	2.50	$\times 10^{-7}$	2.40	$\times 10^{6}$	3.52	$\times 10^{13}$
0.721	3.05		2.63		2.80	
0.757	4.01		2.66		1.95	
0.793	4.81		2.96		1.66	
0.830	6.73		3.15		1.29	

Table 4.3 D Calculated values of $[L]$, $\frac{T_M-[L]X}{[L]^2X}$ and $\frac{T_L-[L]X}{[L]^3X}$ at various values of "a" from pH-metric titration curve of Cd(II) -L-phenylalanine system

a	$[L]$		$\frac{T_M-[L]X}{[L]^2X}$		$\frac{T_L-[L]X}{[L]^3X}$	
0.071	1.08		-3.61		1.88	
0.107	1.24		-3.05		1.58	
0.143	1.41		-2.56		1.40	$\times 10^{15}$
0.179	1.59		-2.11	$\times 10^{7}$	1.30	
0.214	1.85		-1.71		1.07	
0.250	2.13		-1.36		9.29	
0.286	2.51		-1.04		7.59	
0.322	2.94	$\times 10^{-8}$	-7.71		6.32	
0.357	3.36		-5.64	$\times 10^{6}$	5.50	
0.393	4.00		-3.66		4.42	$\times 10^{14}$
0.429	4.75		-2.07		3.56	
0.465	5.61		-7.61		2.91	
0.501	6.59		3.34	$\times 10^{5}$	2.40	
0.536	7.88		1.23		1.92	
0.572	9.58		1.93		1.49	
0.608	1.10		2.67		1.31	
0.644	1.38		3.03		9.64	
0.679	1.67		3.44		7.71	
0.715	2.10	$\times 10^{-7}$	3.63	$\times 10^{6}$	5.72	
0.751	2.71		3.73		4.12	$\times 10^{13}$
0.787	3.42		3.94		3.16	
0.822	4.40		4.12		2.39	
0.858	6.09		4.12		1.62	
0.894	7.54		4.88		1.47	
0.930	1.14	$\times 10^{-6}$	5.25		9.99	$\times 10^{12}$

Table 4.3 E Calculated values of $[L]$, $\frac{T_M-[L]X}{[L]^2X}$ and $\frac{T_L-[L]X}{[L]^3X}$ at various values of "a" from pH-metric titration curve of Cd(II) -L-threonine system

a	$[L]$	$\frac{T_M-[L]X}{[L]^2X}$	$\frac{T_L-[L]X}{[L]^3X}$
0.036	1.26	-3.24	1.16 $\times 10^{15}$
0.071	1.41	-2.80	1.05
0.107	1.57	-2.41	9.83
0.143	1.83	-1.98 $\times 10^{7}$	8.25
0.179	1.97	-1.71	8.38
0.214	2.28	-1.38	7.14
0.250	2.76 $\times 10^{-8}$	-1.05	5.52
0.286	3.17	-8.19	4.79 $\times 10^{14}$
0.322	3.71	-6.05	4.00
0.357	4.44	-4.22 $\times 10^{6}$	3.17
0.393	5.16	-2.77	2.68
0.429	6.41	-1.47	1.98
0.465	7.74	-4.83	1.54
0.501	9.52	2.92 $\times 10^{5}$	1.16
0.536	1.14	8.90	9.26
0.572	1.41	1.39	7.01
0.608	1.66	1.83	5.84
0.644	2.07	2.12	4.38
0.679	2.50 $\times 10^{-7}$	2.40 $\times 10^{6}$	3.52 $\times 10^{13}$
0.715	3.05	2.63	2.80
0.751	4.01	2.66	1.95
0.787	4.81	2.96	1.66
0.822	6.13	3.15	1.29

Table 4.3 F Calculated values of $[L]$, $\frac{T_M-[L]X}{[L]^2X}$ and $\frac{T_L-[L]X}{[L]^3X}$ at various values of "a" from pH-metric titration curve of Cd(II) -L-tryptophan system

a	$[L]$	$\frac{T_M-[L]X}{[L]^2X}$	$\frac{T_L-[L]X}{[L]^3X}$
0.290	1.32	-1.99	2.75
0.326	1.47	-1.54 $\times 10^{7}$	2.54
0.362	1.63	-1.13	2.36
0.399	1.90	-7.41	2.00
0.435	2.14	-4.15	1.79 $\times 10^{15}$
0.471	2.41	-1.22	1.62
0.508	2.76	1.40 $\times 10^{6}$	1.41
0.544	3.22 $\times 10^{-8}$	3.65	1.19
0.580	3.72	5.66	1.02
0.616	4.18	7.73	9.43
0.653	4.98	9.18	7.72
0.689	5.73	1.09	6.84
0.725	6.98	1.20	5.48 $\times 10^{14}$
0.761	8.15	1.36 $\times 10^{7}$	4.84
0.798	9.97	1.49	3.99
0.834	1.21 $\times 10^{-7}$	1.67	3.46
0.870	1.53	1.87	2.88

Table 4.3 G Calculated values of $[L]$, $\frac{T_M-[L]X}{[L]^2X}$ and $\frac{T_L-[L]X}{[L]^3X}$ at various values of "a" from pH-metric titration curve of Cd(II)-L-valine system

a	$[L]$	$\frac{T_M-[L]X}{[L]^2X}$	$\frac{T_L-[L]X}{[L]^3X}$
0.114	1.07	-3.72	1.77
0.132	1.30	-2.92	1.43
0.190	1.49	-2.36 $\times 10^{7}$	1.34 $\times 10^{15}$
0.228	1.71	-1.89	1.21
0.266	2.11	-1.40	9.16
0.304	2.46 $\times 10^{-8}$	-1.06	7.93
0.343	2.86	-7.70	6.84
0.381	3.56	-4.98	5.09 $\times 10^{14}$
0.419	4.20	-2.99 $\times 10^{6}$	4.25
0.457	5.29	-1.26	3.09
0.495	6.63	6.48 $\times 10^{3}$	2.28
0.533	8.07	9.83 $\times 10^{5}$	1.78
0.571	1.04	1.72	1.25
0.609	1.28	2.24	9.60
0.647	1.52	2.78	7.99
0.685	1.87 $\times 10^{-7}$	3.16 $\times 10^{6}$	6.24 $\times 10^{13}$
0.723	2.31	3.51	4.91
0.761	2.74	4.01	4.26
0.799	3.56	4.19	3.14

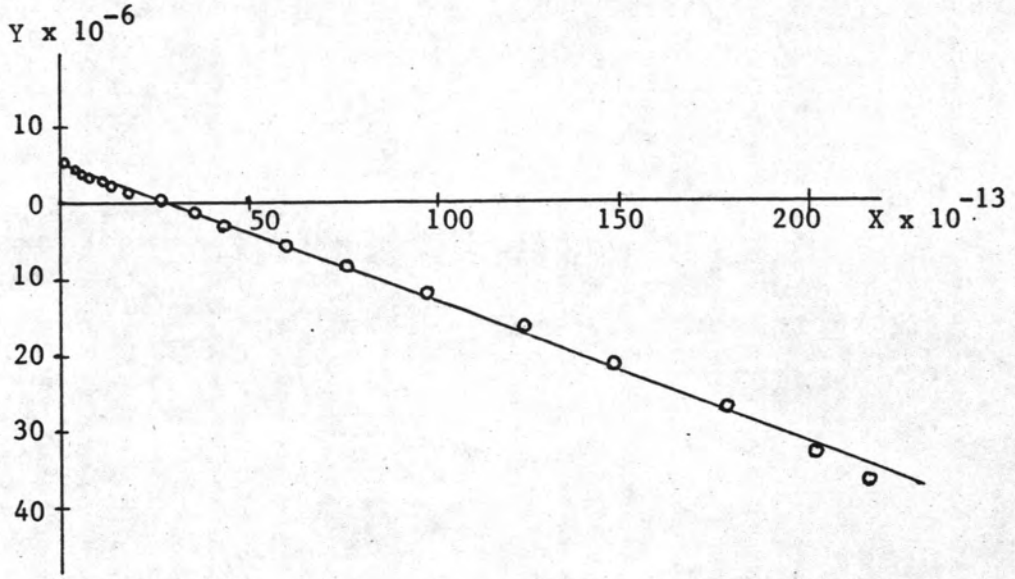

Figure 4.3 A The relationship between $\frac{T_L-[L]X}{[L]^3X}$ (X-axis) and $\frac{T_M-[L]X}{[L]^2X}$ (Y-axis) of Cd(II)-L-isoleucine system

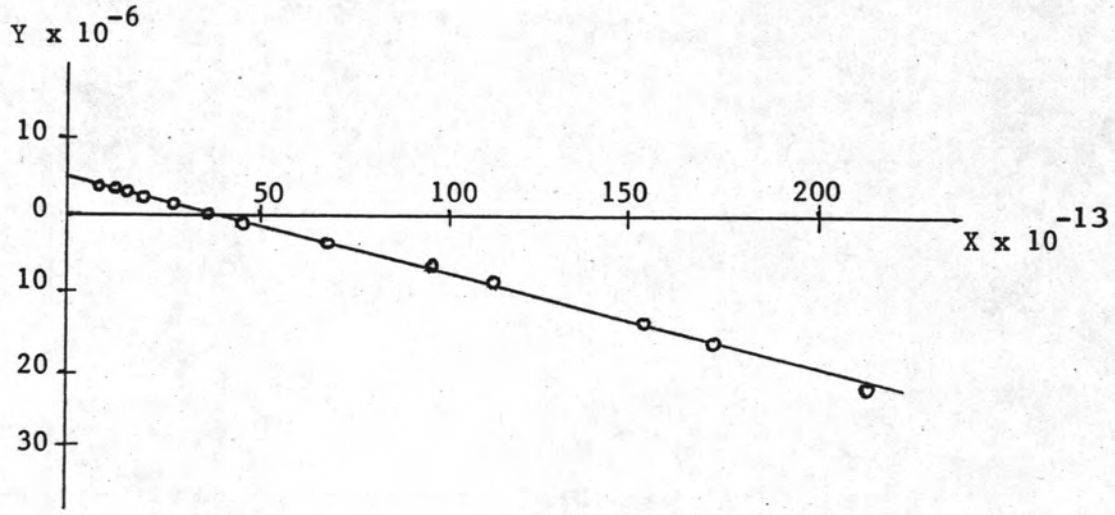

Figure 4.3 B The relationship between $\frac{T_L-[L]X}{L^3X}$ (X-axis) and $\frac{T_M-[L]X}{[L]^2X}$ (Y - axis) of Cd(II)-L-leucine system

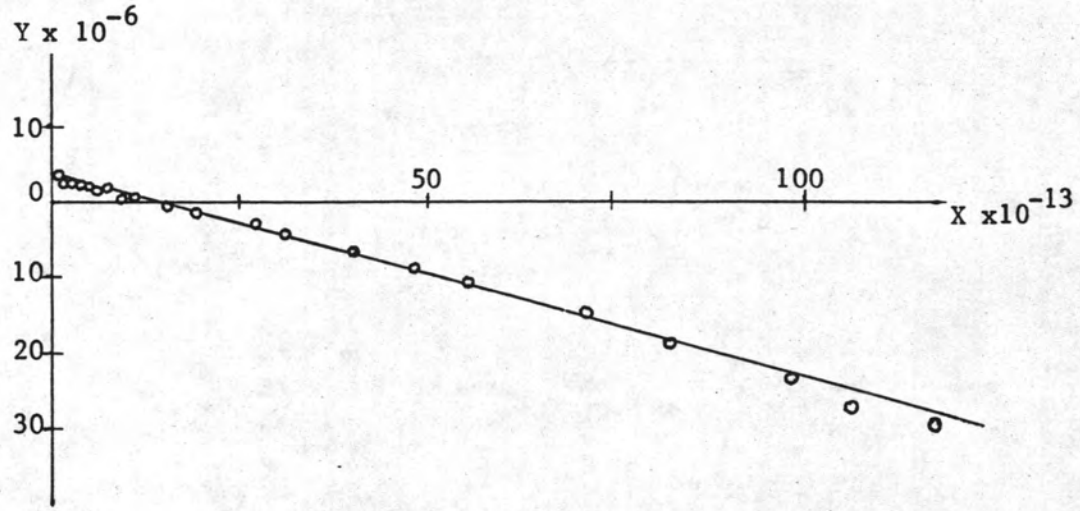

Figure 4.3 C The relationship between $\frac{T_L-[L]X}{[L]^3X}$ (X-axis) and $\frac{T_M-[L]X}{[L]^2X}$ (Y-axis) of Cd(II)-L-methionine system

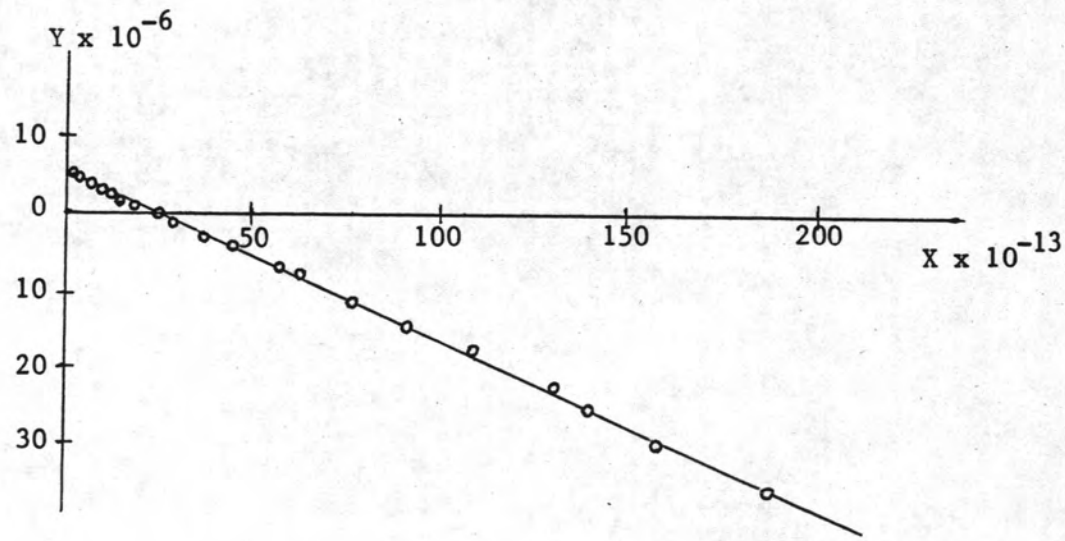

Figure 4.3 D The relationship between $\frac{T_L-[L]X}{[L]^3X}$ (X-axis) and $\frac{T_M-[L]X}{[L]^2X}$ (Y-axis) of Cd(II)-L-phenylalanine system

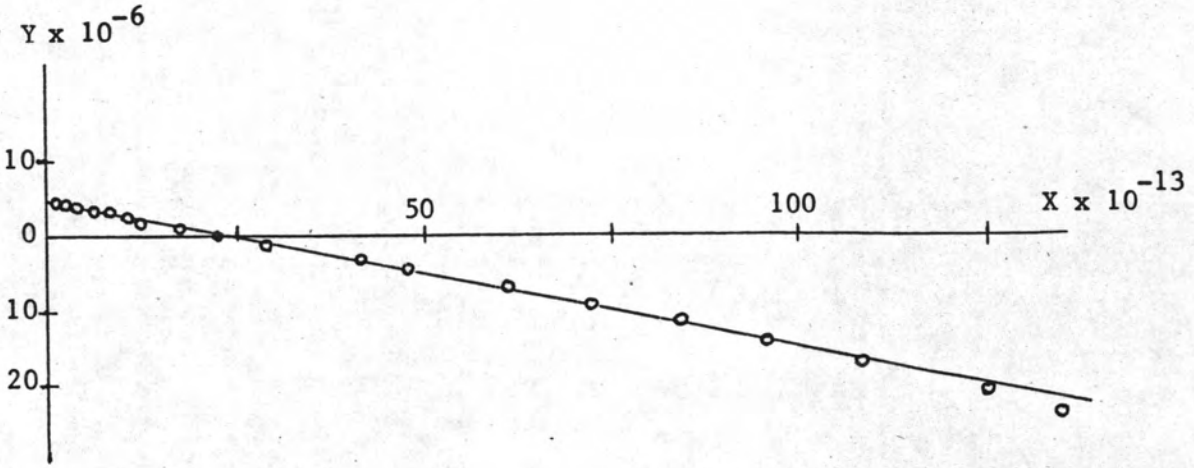

Figure 4.3 E The relationship between $\frac{T_L-[L]X}{[L]^3X}$ (X-axis) and $\frac{T_M-[L]X}{[L]^2X}$ (Y-axis) of Cd(II) -L-threonine system

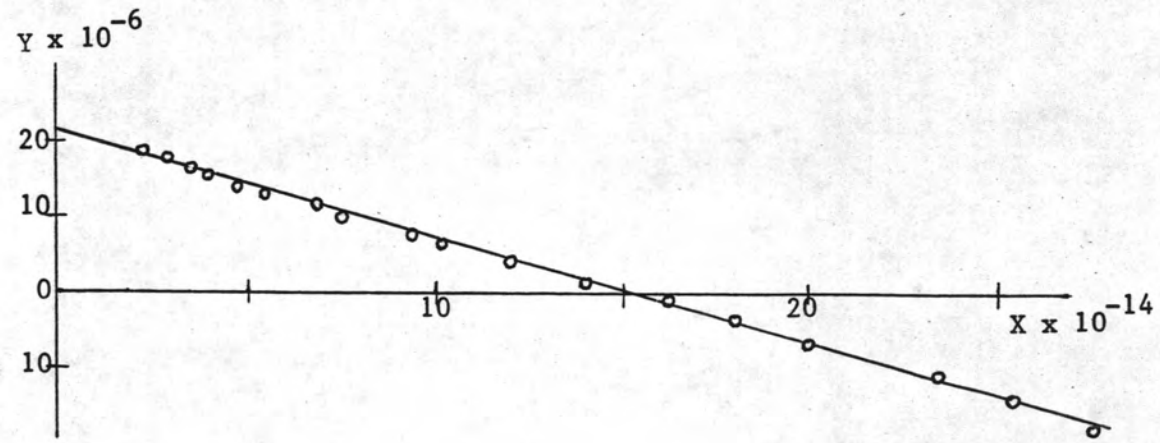

Figure 4.3 F The relationship between $\frac{T_L-[L]X}{[L]^3X}$ (X-axis) and $\frac{T_M-[L]X}{[L]^2X}$ (Y-axis) of Cd(II)-L-tryptophan system

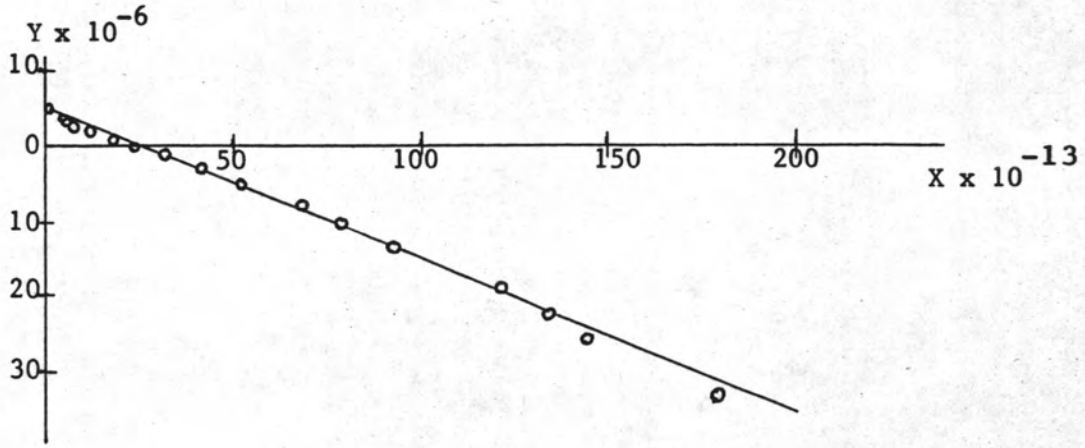

Figure 4.3 G The relationship between $\frac{T_L-[L]X}{[L]^3X}$ (X-axis) and $\frac{T_M-[L]X}{[L]^2X}$ (Y-axis) of Cd(II) -L-valine system

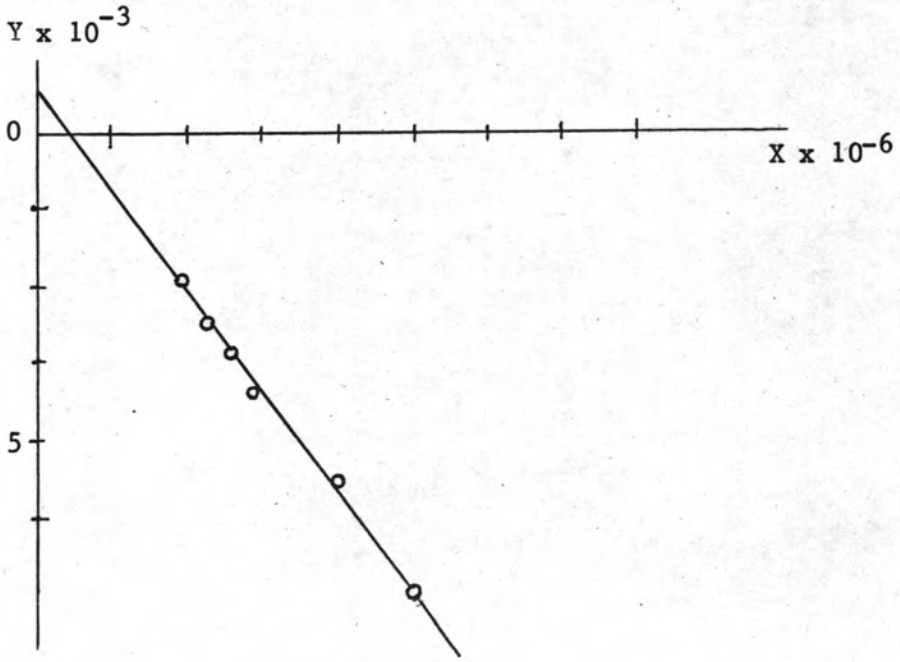

Figure 4.4 A The relationship between $\frac{T_L-[L]X}{[L]^3X}$ (X-axis) and $\frac{T_M-[L]X}{[L]^2X}$ (Y-axis) of Mn(II) -L-isoleucine system

Table 4.4 The linear correlation between $\frac{T_L-[L]X}{[L]^3X}$ and $\frac{T_M-[L]X}{[L]^2X}$ and the stability constants of Cd(II) -essential amino acid complexes by pH-metric titration technique

anion of Cd complex	linear correlation coefficient (γ)	Stability Constants				Remarks
		K_1	log K_1	K_2	log K_2	
L-isoleucine	0.990	5.12×10^7	7.71	5.23×10^6	6.72	
L-leucine	0.996	7.88×10^7	7.90	5.37×10^6	6.73	
L-lysine	-	-	-	-	-	precipitatio
L-methionine	0.990	3.49×10^7	7.54	4.08×10^6	6.61	
L-phenylalanine	0.998	4.64×10^7	7.67	5.29×10^6	6.72	
L-threonine	0.996	4.99×10^7	7.70	4.20×10^6	6.62	
L-tryptophan	0.996	6.98×10^7	7.84	2.10×10^7	7.32	
L-valine	0.990	4.48×10^7	7.65	5.35×10^6	6.73	

4.3.2 Mn(II)-Essential Amino Acid Systems

No physical change was observed after adding the solution of 5.00×10^{-4} M Mn(II) ion into the solution of 1.00×10^{-3} M essential amino acid and the mixture still colorless for all systems. Each solution of 1.00×10^{-3} M essential amino acid in the presence of 5.00×10^{-4} M Mn(II) ion at the same condition mentioned above was titrated against the standard NaOH solution and the pH-values were recorded for each addition of NaOH. The pH-metric titration data are illustrated respectively for the systems of Mn(II)-L-isoleucine, Mn(II)-L-leucine, Mn(II)-L-lysine, Mn(II)-L-methionine, Mn(II)-L-phenylalanine, Mn(II)-L-threonine, Mn(II)-L-tryptophan and Mn(II)-L-valine in Appendix 3A-3H. The gray precipitate occurred during the titration of Mn(II)-L-lysine system at pH 8.52 (see Appendix 3C) and the precipitate was dispersed in the solution. The plots of "a" versus resulting pH gave the pH-metric titration curve of each Mn(II)-essential amino acid system as shown respectively by curve 4 in Figure 4.1 A - 4.1 H. Unclear infleciton was all observed on the pH-metric titration curve, but the evidence such as no occurring of precipitate during the titration indicated that the formation of the complexes was taken place in the solution of Mn(II)-essential amino acid systems. Therefore, the pH-metric titration curves of Mn(II)-essential amino acid systems were analyzed as the preceding section, excepted of Mn(II)-L-lysine system. The calculated corresponding values of a, $[L]$, $\frac{T_M - [L]X}{[L]^2 X}$ and $\frac{T_L - [L]X}{[L]^3 X}$ of the systems of Mn(II)-L-isoleucine, Mn(II)-L-leucine, Mn(II)-L-methionine, Mn(II)-L-phenylalanine, Mn(II)-L-threonine, Mn(II)-L-tryptophan and Mn(II)-L-valine are shown respectively in Table 4.5 A -

4.5 G. The plots of $\frac{T_L - [L]\ X}{[L]^3 X}$ versus $\frac{T_M - [L]\ X}{[L]^2 X}$ by least squares method gave the linear portion of these systems (see Figure 4.4 A - 4.4 G). The negative slope was all found from the linearity of Mn(II)-essential amino acid systems, but the positive intercept was only found from the linearity of Mn(II)-L-isoleucine and Mn(II)-L-tryptophan systems (see Figure 4.4 A - 4.4 G). By equation (2.18), the values of both stepwise stability constants, K_1 and K_2, were provided for the complexes of Mn(II)-L-isoleucine and Mn(II)-L-tryptophan and the values of K_1 only were provided for the complexes of Mn(II)-L-leucine, Mn(II)-L-methionine, Mn(II)-L-phenylalanine, Mn(II)-L-threonine and Mn(II)-L-valine. From the obtained values of the stepwise stability constants and the structure of the essential amino acids, it can be said that the composition of the 1:2 complexes of Mn(II) ion to L-isoleucine and Mn(II) ion to L-tryptophan was probably indicated in stepwise formation from the 1:1 complexes and the composition of the 1:1 complesès of Mn(II) ion to L-leucine, Mn(II) ion to L-methionine, Mn(II) ion to L-phenylalanine, Mn(II) ion to L-threonine and Mn(II) ion to L-valine was probably indicated in the solution. The values of the linear correlation coefficient (γ) for each linearity of the Mn(II)-essential amino acid complexes including K_1, log K_1, K_2 and log K_2 of their complexes are listed in Table 4.6.

4.3.3 Pb(II)-Essential Amino Acid Systems

After adding the solution of 5.00×10^{-4} M Pb(II) ion into the solution of 1.00×10^{-3} M essential amino acid, no physical

Table 4.5 A Calculated values of $[L]$, $\frac{T_M-[L]X}{[L]^2X}$ and $\frac{T_L-[L]X}{[L]^3X}$ at various values of "a" from pH-metric titration curve of Mn(II)-L-isoleucine system

a	$[L]$	$\frac{T_M-[L]X}{[L]^2X}$	$\frac{T_L-[L]X}{[L]^3X}$
0.114	7.97 $\times 10^{-5}$	-6.08	4.86
0.152	1.05	-4.56	3.89
0.190	1.35 $\times 10^{-4}$	-3.52	2.70 $\times 10^{6}$
0.228	1.58	-2.96 $\times 10^{3}$	2.53
0.266	1.81	-2.56	2.26
0.343	2.29	-1.97	1.89

Table 4.5 B Calculated values of $[L]$, $\frac{T_M - [L]X}{[L]^2 X}$ and $\frac{T_L - [L]X}{[L]^3 X}$ at various values of "a" from pH-metric titration curve of Mn(II) -L-leucine system

a	$[L]$		$\frac{T_M - [L]X}{[L]^2 X}$		$\frac{T_L - [L]X}{[L]^3 X}$	
0.145	9.48	$\times 10^{-5}$	-5.01		5.08	
0.181	1.22		-3.87		3.67	
0.217	1.50		-3.13		2.69	
0.253	1.76		-2.65		2.19	
0.289	2.07	$\times 10^{-4}$	-2.26	$\times 10^{3}$	1.52	$\times 10^{6}$
0.325	2.30		-2.00		1.49	
0.362	2.51		-1.81		1.42	
0.398	2.72		-1.65		1.40	
0.434	2.95		-1.50		1.28	

Table 4.5 C Calculated values of $[L]$, $\frac{T_M-[L]X}{[L]^2X}$ and $\frac{T_L-[L]X}{[L]^3X}$ at various values of "a" from pH-metric titration curve of Mn (II) -L-methionine system

a	$[L]$	$\frac{T_M-[L]X}{[L]^2X}$	$\frac{T_L-[L]X}{[L]^3X}$
0.252	1.99	-2.40	1.18
0.288	2.27	-2.08	1.03
0.325	2.47	-1.89	1.12
0.361	2.74	-1.69	1.00
0.397	3.04	-1.52	8.31
0.433	3.28	-1.39	8.04
	$\times 10^{-4}$	$\times 10^{3}$	$\times 10^{6}$ (rows 1–4), $\times 10^{5}$ (rows 5–6)

Table 4.5 D Calculated values of $[L]$, $\frac{T_M - [L]X}{[L]^2 X}$ and $\frac{T_L - [L]X}{[L]^3 X}$ at various values of "a" from pH-metric titration curve of Mn(II) -L-phenylalanine system

a	$[L]$	$\frac{T_M - [L]X}{[L]^2 X}$	$\frac{T_L - [L]X}{[L]^3 X}$
0.143	8.71 $\times 10^{-5}$	-5.42	7.36
0.179	1.12	-4.16	5.46
0.214	1.41	-3.29	3.66
0.250	1.62	-2.83	3.21
0.286	1.89	-2.40	2.62
0.322	2.15 $\times 10^{-4}$	-2.08 $\times 10^{3}$	2.24 $\times 10^{6}$
0.357	2.34	-1.88	2.17
0.393	2.59	1.68	1.93
0.429	2.79	-1.53	1.89
0.465	3.01	-1.40	1.75
0.501	3.22	-1.28	1.69

Table 4.5 E Calculated values of $[L]$, $\frac{T_M - [L]X}{[L]^2 X}$ and $\frac{T_L - [L]X}{[L]^3 X}$ at various values of "a" from pH-metric titration curve of Mn(II)-L-threonine system

a	$[L]$	$\frac{T_M - [L]X}{[L]^2 X}$	$\frac{T_L - [L]X}{[L]^3 X}$
0.072	4.78 $\times 10^{-5}$	-1.02 $\times 10^{4}$	1.01 $\times 10^{7}$
0.108	7.59 $\times 10^{-5}$	-6.38 $\times 10^{3}$	5.47 $\times 10^{6}$
0.144	1.02 $\times 10^{-4}$	-4.68	4.40
0.180	1.32	-3.61	2.65
0.216	1.62	-2.93	1.95
0.252	1.85	-2.53	1.90
0.288	2.07	-2.23	1.77
0.325	2.41	-1.92	1.30
0.361	2.61	-1.74	1.35
0.397	2.82	-1.58	1.35
0.433	3.11	-1.43	1.16

Table 4.5 F Calculated values of $[L]$, $\frac{T_M-[L]X}{[L]^2X}$ and $\frac{T_L-[L]X}{[L]^3X}$ at various values of "a" from pH-metric titration curve of Mn(II) -L-tryptophan system

a	$[L]$	$\frac{T_M-[L]X}{[L]^2X}$	$\frac{T_L-[L]X}{[L]^3X}$
0.145	9.98×10^{-5}	-4.80×10^{3}	4.08×10^{6}
0.181	1.26×10^{-4}	-3.78	3.12
0.217	1.51	-3.12	2.56
0.254	1.73	-2.68	2.39
0.290	2.02	-2.28	1.83
0.326	2.20	-2.06	1.91
0.362	2.51	-1.80	1.48

Table 4.5 G Calculated values of $[L]$, $\frac{T_M-[L]X}{[L]^2X}$ and $\frac{T_L-[L]X}{[L]^3X}$ at various values of "a" from pH-metric titration curve of Mn(II)-L-valine system

a	$[L]$	$\frac{T_M-[L]X}{[L]^2X}$	$\frac{T_L-[L]X}{[L]^3X}$
0.076	6.00×10^{-5}	-8.22×10^{3}	3.69×10^{6}
0.114	9.09×10^{-5}	-5.39	2.34
0.152	1.28×10^{-4}	-3.82	1.26
0.190	1.61	-3.04	8.59×10^{5}
0.228	1.89	-2.57	7.68
0.266	2.16	-2.23	7.51

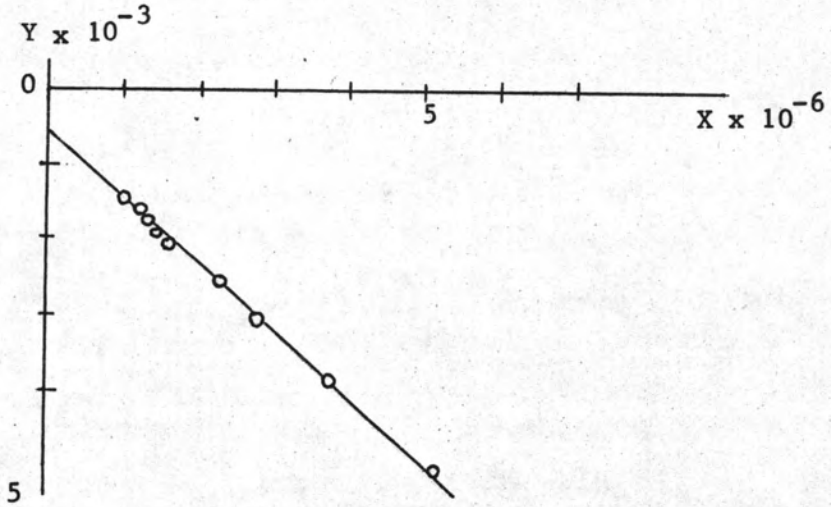

Figure 4.4 B The relationship between $\frac{T_L-[L]X}{[L]^3X}$ (X-axis) and $\frac{T_M-[L]X}{[L]^2X}$ (Y-axis) of Mn(II)-L-leucine system

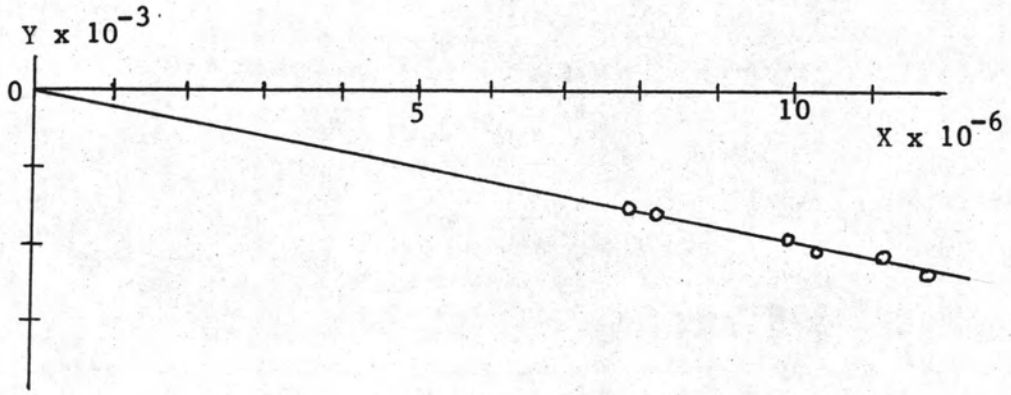

Figure 4.4 C The relationship between $\frac{T_L-[L]X}{[L]^3X}$ (X-axis) and $\frac{T_M-[L]X}{[L]^{2X}}$ (Y-axis) of Mn(II) -L-methionine system

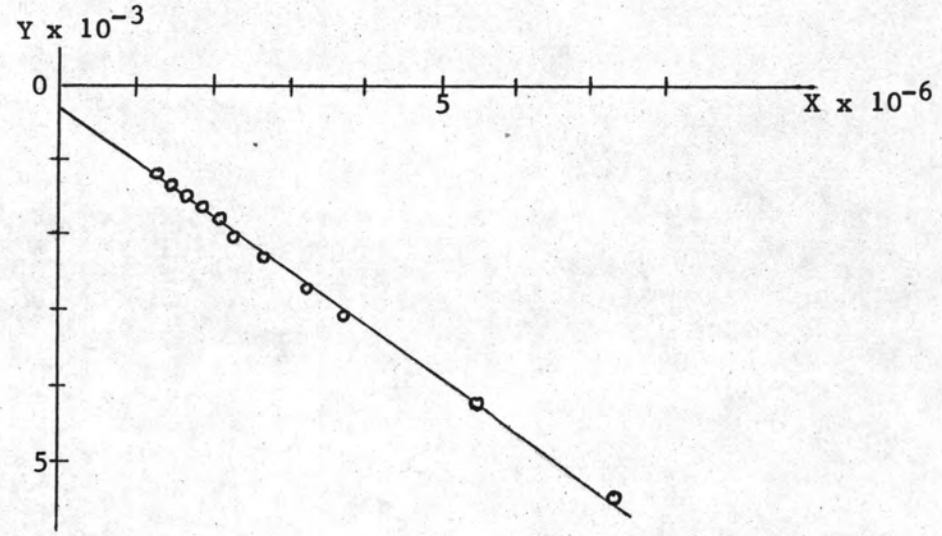

Figure 4.4 D The relationship between $\frac{T_L-[L]X}{[L]^{3X}}$ (X-axis) and $\frac{T_M-[L]X}{[L]^{2}X}$ (Y-axis) of Mn(II)-L-phenylalanine system

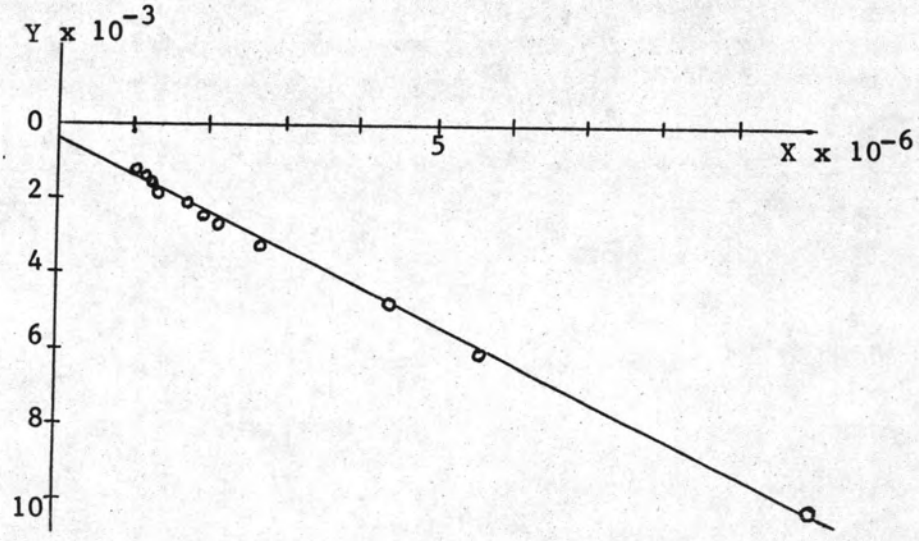

Figure 4.4 E The relationship between $\frac{T_L[L]X}{[L]^{3}X}$ (X-axis) and $\frac{T_M-[L]X}{[L]^{2}X}$ (Y-axis) of Mn (II) -L-threonine system

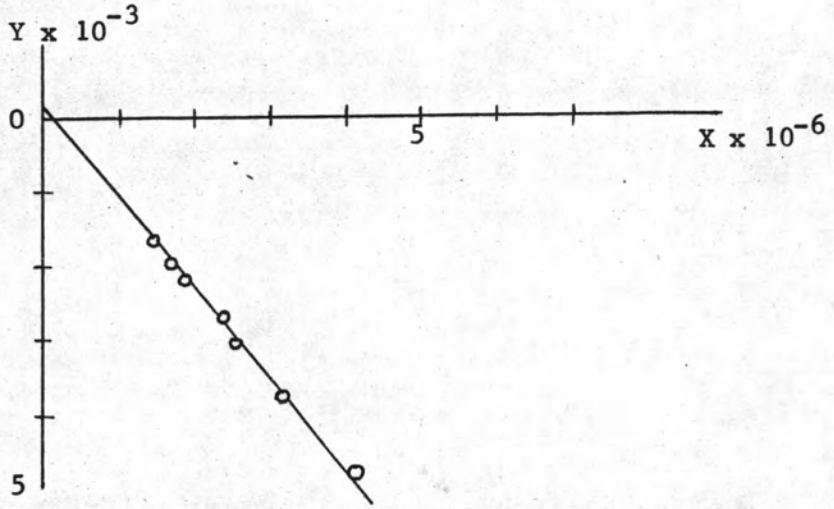

Figure 4.4 F The relationship between $\frac{T_L[L]X}{[L]^2X}$ (X -axis) and $\frac{T_M-[L]X}{[L]^2X}$ (Y-axis) of Mn(II) -L-tryptophan system

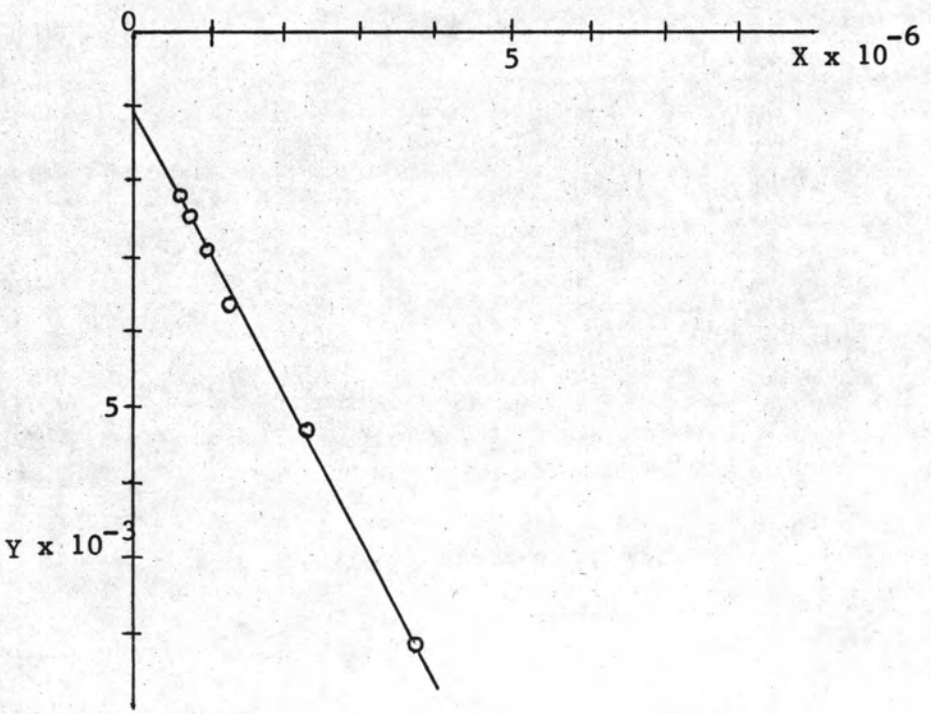

Figure 4.4 G The relationship between $\frac{T_L-[L]X}{[L]^3X}$ (x-axis) and $\frac{T_M-[L]X}{[L]^2X}$ (Y-axis) of Mn (II) -L-valine system

Table 4.6 The linear correlation between $\frac{T_L-[L]X}{[L]^3X}$ and $\frac{T_M-[L]X}{[L]^2X}$ and the stability constants of Mn (II) -essential amino acid complexes by pH-metric titration technique

anion of Mn complex	linear correlation coefficient (γ)	Stability Constants				Remarks
		K_1	log K_1	K_2	log K_2	
L-isoleucine	0.994	7.57×10^2	2.88	3.81×10^2	2.58	
L-leucine	0.996	1.13×10^3	3.05	-	-	
L-lysine	-	-	-	-	-	precipitation
L-methionine	0.855	5.65×10^2	2.75	-	-	
L-phenylalanine	0.989	1.40×10^3	3.15	-	-	
L-threonine	0.996	1.03×10^3	3.01	-	-	
L-tryptophan	0.988	8.19×10^2	2.91	0.84×10^2	1.93	
L-valine	0.992	5.26×10^2	2.72	-	-	

change was observed and the mixture still colorless for all systems. Each solution of 1.00×10^{-3} M essential amino acid in the presence of 5.00×10^{-4} M Pb(II) ion at the same conditions mentioned above was titrated against the standard solution of NaOH. The pH-metric titration data of the systems of Pb(II)-L-methionine, Pb(II)-L-leucine, Pb(II)-L-lysine, Pb(II)-L-methionine, Pb(II)-l-phenylalanine, Pb(II) -L-threonine, Pb(II)-L-tryptophan and Pb(II)-L-valine are shown respecitvely in Appendix 4A-4H. The occurrence of the white gelatineous precipitate dispersed in the solution during the titration was found at about pH 7 of all systems and the pH-metric titration can not be performed further because the pH-readings were interfered by the precipitate. Therefore, the incomplete pH-metric titration curves of Pb(II)-essential amino acid systems were obtained as shown by curve 5 in Figure 4.1 A - 4.1 H. It can be said that the occurring of precipitate during the titration indicated the complex formation was not taken place in the solution of Pb(II)-essential amino acid systems by the pH-metric titration analysis.

4.4 Complex Formation by Polarographic Technique

The complex formations of interesting ions, Cd(II), Mn(II) and Pb(II) ion, with essential amino acids were also determined carefully by polarographic technique. The experimental conditions used were the same as those mentioned in pH-metric titration technique, the constant ionic strength of 0.10 M KCl and the constant temperature of $37.0 \pm 0.5^{\circ}C$

4.4.1 Polarographic Behavior of the Essential Amino Acids

Polarographic studies of all essential amino acids were

performed in the concentration range of 1.00×10^{-1} - 5.00×10^{-6} M, the pH range of 3.01 - 10.97 by means of the Michaelis borate buffer solution and 0.10 M KCl supporting electrolyte solution. No reduction wave of all solutions mentioned above was resulted in the voltage range of (0.000)-(-3.000) volts as shown in Figure 4.5 Therefore, these essential amino acids are inert in the polarographic mode.

4.4.2 Polarographic Behavior of the Complexes

Each solution containing 1.00×10^{-4} M metal ion in the presence of 4.00×10^{-4} - 1.00×10^{-1} M essential amino acid at the constant ionic strength of 0.10 M KCl (supporting electrolyte solution) and the constant temperature of 37.0 ± 0.5°C was polarographically studied as followings; (i) varying pH of the solutions in the range of 3.01 - 10.97 by means of the Michaelis borate buffer at a constant concentration of the essential amino acid, (ii) varying the essential amino acid concentrations in the range of 4.00×10^{-4} - 1.00×10^{-1} M at a constant pH and (iii) varying the heights of Hg-reservior in the range of 40.0 - 70.0 cm at a constant pH and a constant concentration of the essential amino acid.

4.4.2.1 Cd(II)-Essential Amino Acid Systems

The solutions containing 1.00×10^{-4} M Cd(II) ion in the presence of 4.00×10^{-4} M essential amino acid were studied at several pH values. The effects of pH on the polarographic characteristics such as $E_{\frac{1}{2}}$, i_d and $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ of the systems of Cd(II)-L-isoleucine, Cd(II)-L-leucine, Cd(II)-L-lysine, Cd(II)-methionine, Cd(II)-L-phenylalanine, Cd(II)-L-threonine, Cd(II)-L-tryptophan and Cd(II)-valine are shown respectively, in Table 4.7 A - 4.7 H and the

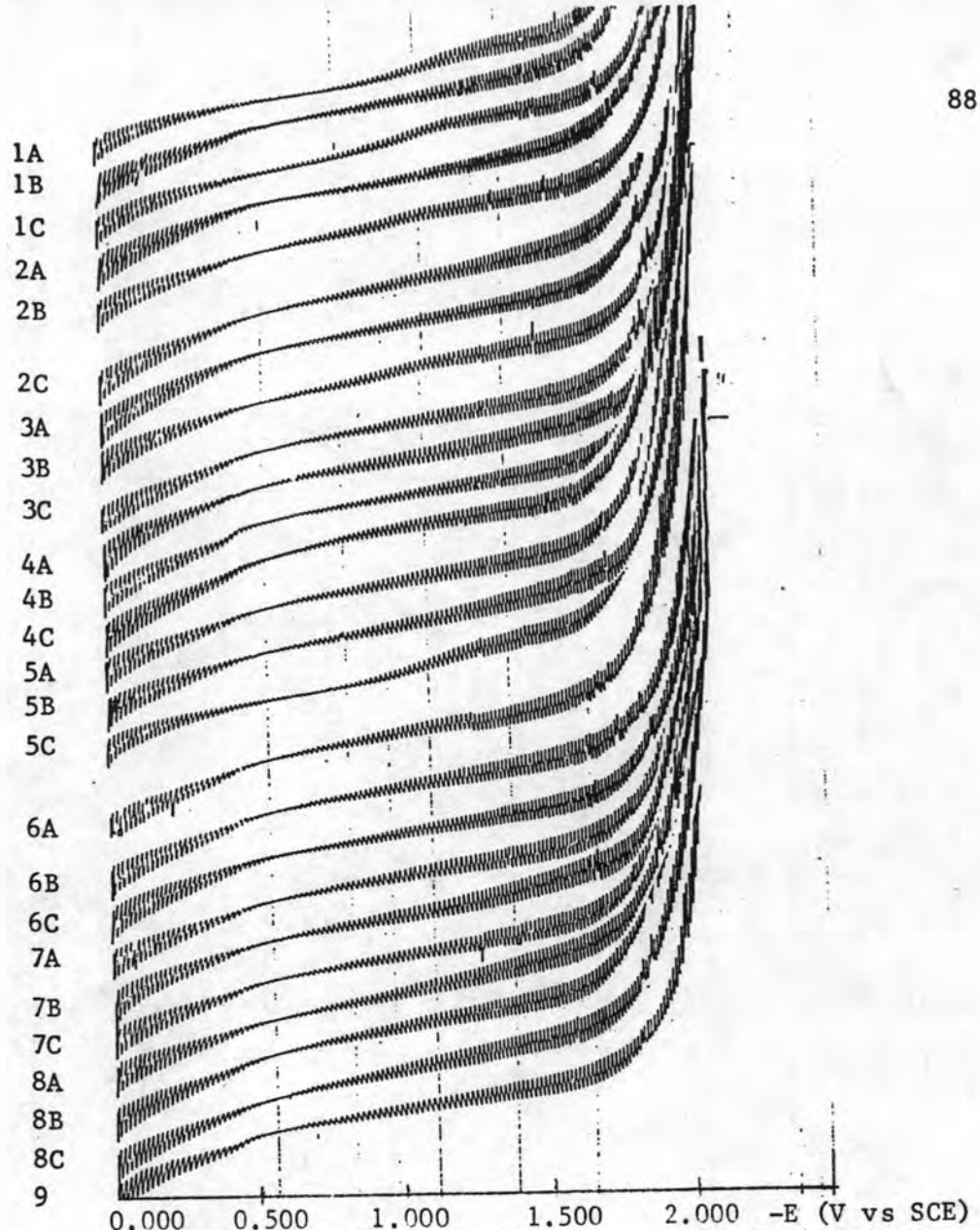

Figure 4.5 Polarograms of the essential amino acids in 0.10 M KCl and borate buffer;

1)L-isoleucine at 1A)5.00×10^{-4}M pH 4.30, 1B)1.00×10^{-3}M pH 7.10, 1C)1.00×10^{-4} M pH 8.90

2)L-leucine at 2A) 5.00×10^{-2} M pH 4.40, 2B) 5.00×10^{-4} M pH 6.75 2C) 1.00×10^{-4} M pH 8.85

3)L-lysine at 3A) 5.00×10^{-4} M pH 4.10, 3B) 1.00×10^{-4} M pH 7.15, 3C) 5.00×10^{-3} M pH 9.10

4)L-methionine at 4A) 1.00×10^{-2} MpH 4.70, 4B) 5.00×10^{-4} M pH 7.43, 4C) 5.00×10^{-2} M pH 8.89

5)L-phenylalanine at 5A) 5.00×10^{-4} M pH 4.32, 5B) 5.00×10^{-3}M pH 6.87, 5C) 1.00×10^{-4} M pH 8.25

6)L-threonine at 6A) 1.00×10^{-3} M pH 4.72, 6B) 5.00×10^{-3} M pH 7.54, 6C) 1.00×10^{-4} M pH 8.78

7)L-tryptophan at 7A)5.00×10^{-4} M pH 4.31, 7B) 5.00×10^{-3} M pH 7.43, 7C) 5.00×10^{-2} M pH 8.57

8)L-valine at 8A) 5.00×10^{-3} M pH 4.78, 8B) 1.00×10^{-4} M pH 7.65, 8C) 5.00×10^{-4} M pH 8.26 and 9) the polarogram of supporting electrolyte (0.10 M KCl)

Table 4.7 A Effects of pH on the polarographic characteristics of Cd(II) -L-isoleucine system

pH	$-E_{1/2}$ (V vs SCE)	i_d (μA)	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$ (V)
4.03	0.795	1.98	0.030
5.07	0.797	1.96	0.030
5.93	0.799	1.93	0.031
7.45	0.798	1.90	0.031
8.53	0.815	1.73	0.058

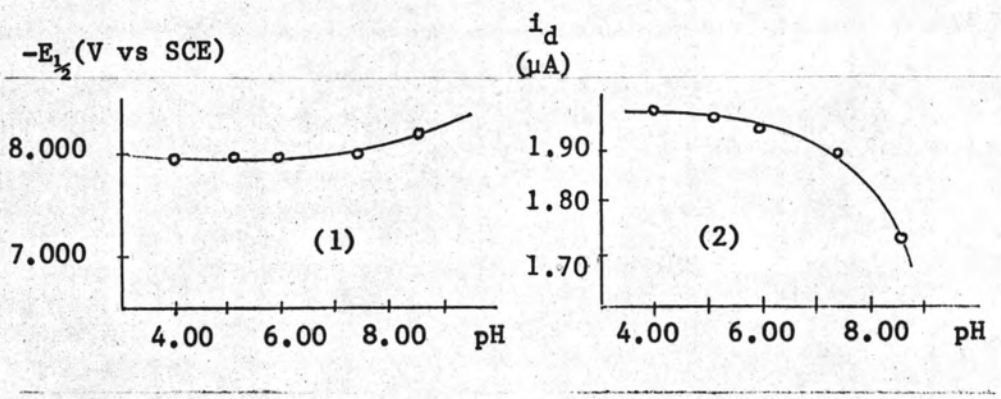

Figure 4.6 A Dependences of pH on $E_{1/2}$ (1) and i_d (2) of Cd (II) -L-isoleucine system

Table 4.7 B Effects of pH on the polarographic characteristics of Cd(II) -L-leucine system

pH	$-E_{\frac{1}{2}}$ (V vs SCE)	i_d (μA)	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$ (V)
3.98	0.789	1.94	0.031
5.04	0.793	1.95	0.031
6.01	0.795	1.94	0.032
7.01	0.790	1.94	0.032
7.46	0.796	1.93	0.032
7.98	0.810	1.54	0.038
8.97	0.824	1.46	0.056

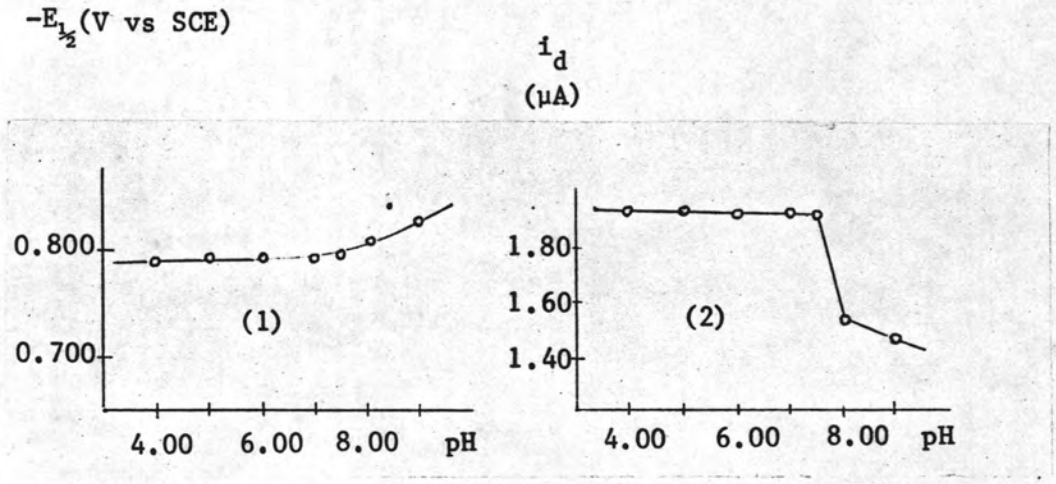

Figure 4.6 B Dependences of pH $E_{\frac{1}{2}}$ (1) and i_d (2) of Cd(II) -L-leucine system

Table 4.7 C Effects of pH on the polarographic characteristics of Cd(II) -L-lysine system

pH	$-E_{1/2}$ (V vs SCE)	i_d (μA)	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$ (V)
2.96	0.745	1.95	0.043
4.12	0.747	1.90	0.030
5.09	0.753	1.85	0.030
6.16	0.748	1.73	0.031
7.01	0.755	1.65	0.031
7.45	0.757	1.61	0.031
8.03	0.763	1.23	0.038
8.98	0.785	1.16	0.058

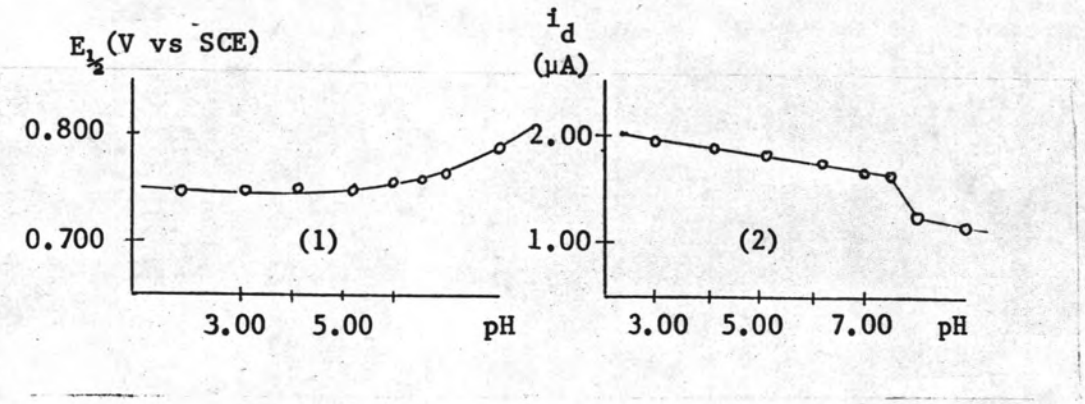

Figure 4.6 C Dependences of pH on $E_{1/2}$ (1) and i_d (2) of Cd(II) -L-lysine system

Table 4.7 D Effects of pH on the polarographic characteristics of Cd(II) -L-methionine system

pH	$-E_{1/2}$ (V vs SCE)	i_d (μA)	$E_{3/4}-E_{1/4}$ (V)
2.85	0.812	2.00	0.031
3.95	0.811	1.98	0.030
5.05	0.810	1.97	0.032
5.65	0.818	1.92	0.032
5.90	0.815	1.89	0.032
6.79	0.820	1.85	0.032
7.44	0.824	1.81	0.032
7.98	0.830	1.70	0.042

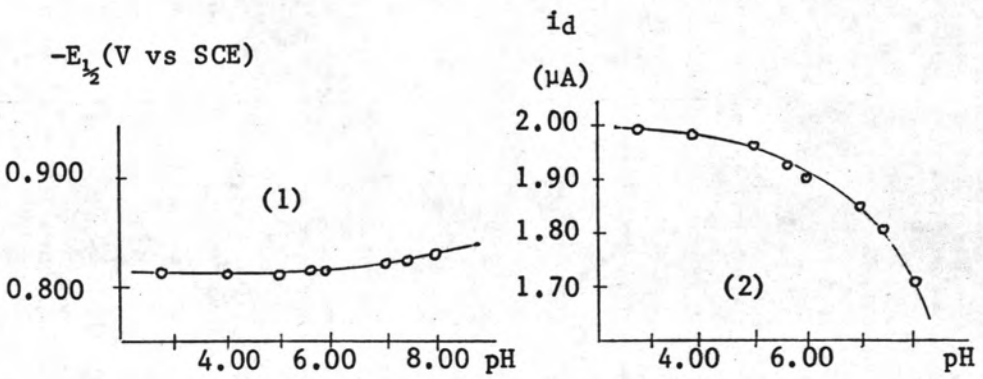

Figure 4.6 D Dependences of pH on $E_{1/2}$ (1) and i_d (2) of Cd(II) -L-methionine system

Table 4.7 E Effects of pH on the polarographic characteristics of Cd(II)-L-phenylalanine system

pH	$-E_{1/2}$ (V vs SCE)	i_d (μA)	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$ (V)
2.88	0.820	1.85	0.030
3.97	0.818	1.88	0.031
4.96	0.819	1.86	0.032
6.01	0.823	1.88	0.032
7.01	0.822	1.84	0.030
7.42	0.822	1.79	0.032
7.96	0.833	1.46	0.040
9.02	0.860	1.33	0.046
10.47	0.879	1.23	0.054

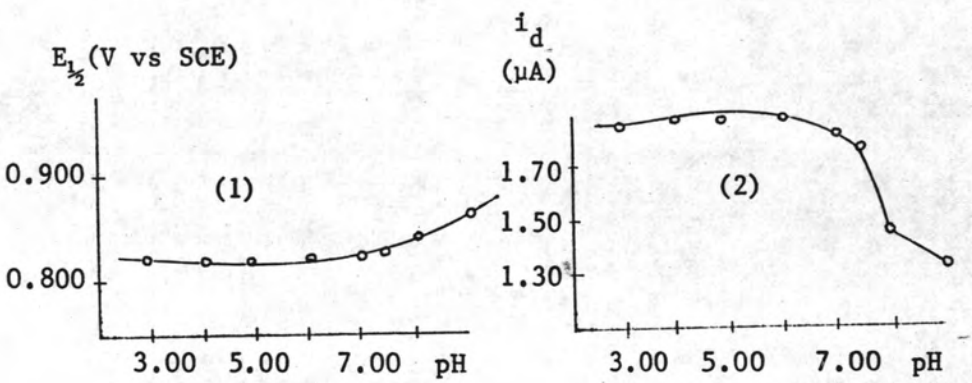

Figure 4.6 E Dependences of pH on $E_{1/2}$ (1) and i_d (2) of Cd (II) -L- phenylalanine system

Table 4.7 F Effects of pH on the polarographic characteristics of Cd(II) -L-threonine system

pH	$-E_{1/2}$ (V vs SCE)	i_d (μA)	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$ (V)
4.00	0.826	1.72	0.030
5.29	0.828	1.70	0.031
7.41	0.830	1.63	0.031
8.46	0.832	1.31	0.031

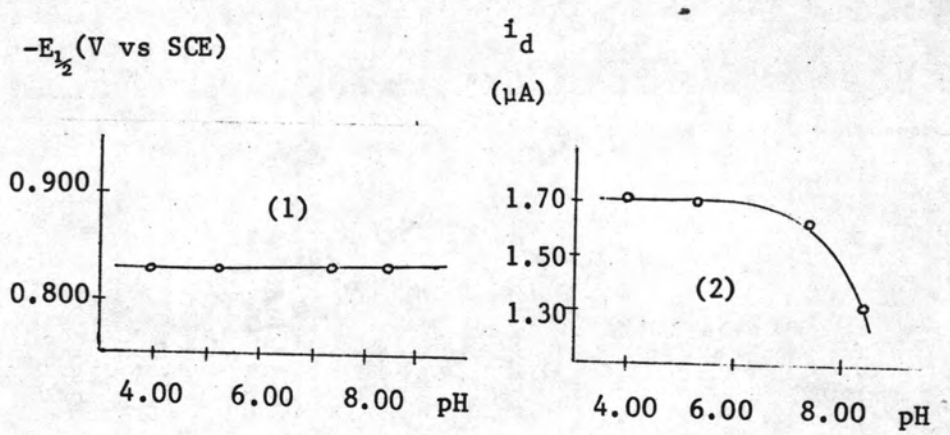

Figure 4.6 F Dependences of pH on $E_{1/2}$ (1) and i_d (2) of Cd(II) -L- threonine system

Table 4.7 G Effects of pH on the polarographic characteristics of Cd(II) -L-tryptophan system

pH	$-E_{1/2}$ (V vs SCE)	i_d (μA)	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$ (V)
3.92	0.830	1.93	O.030
5.03	0.825	1.89	O.030
6.10	0.832	1.90	O.031
7.43	0.838	1.89	O.031
8.05	0.858	1.87	O.031
8.96	0.885	1.63	O.038

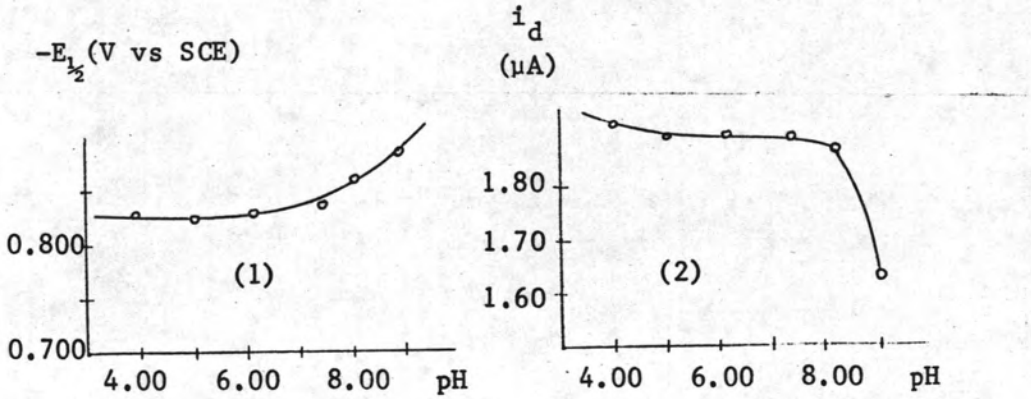

Figure 4.6 G Dependences of pH on $E_{1/2}$ (1) and i_d (2) of Cd (II) -L-tryptophan system

Table 4.7 H Effects of pH on the polarographic characteristics of Cd(II) -L-valine system

pH	$-E_{1/2}$ (V vs SCE)	i_d (μA)	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$ (V)
3.98	0.788	1.85	0.031
5.03	0.790	1.83	0.030
6.00	0.793	1.81	0.030
6.28	0.796	1.79	0.030
7.04	0.798	1.77	0.031
7.42	0.805	1.76	0.031
8.03	0.810	1.23	0.040
9.17	0.823	1.15	0.046

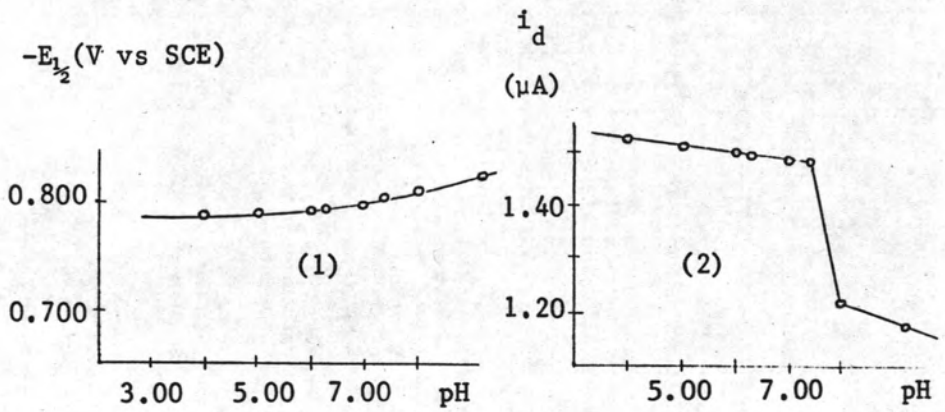

Figure 4.6 H Dependences of pH on $E_{1/2}$ (1) and i_d (2) of Cd (II) -L-valine system

dependences of pH on the polarographic characteristics, $E_{\frac{1}{2}}$ vs pH and i_d vs pH, were plotted as shown respectively for each system in Figure 4.6 A - 4.6 H. As pH increased the i_d decreased and the negative shift in $E_{\frac{1}{2}}$ increased for all systems (see Table 4.7 A - 4.7 H and Figure 4.6 A - 4.6 H). The electrode reaction evaluated from $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ showed the reductions of all systems were reversible in the range of pH 3-8, but they became irreversible at pH above 8. (see Table 4.7 A - 4.7 H). Hence, the neutral pH, pH 7.4, was chosen for studying the complex formation of Cd(II)-essential amino acid systems. At the constant pH, pH 7.4, the solutions containing 1.00×10^{-4} M Cd(II) ion in the presence of essential amino acids were studied by varying the essential amino acid concentrations in the range of 4.00×10^{-4} - 1.00×10^{-1} M. The effects of the essential amino acid concentrations on the polarographic characteristics such as $E_{\frac{1}{2}}$, $\Delta E_{\frac{1}{2}}$, i_d and $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ of the systems of Cd(II)-L-isoleucine, Cd(II)-L-leucine, Cd(II)-L-lysine, Cd(II)-L-methionine, Cd(II)-L-phenylalanine, Cd(II)-threonine, Cd(II)-L-tryptophan and Cd(II)-L-valine are shown respectively in Table 4.8 A - 4.8 H. $[HL]$ and $[L]$ as seen in Table 4.8 A - 4.8 H represented the essential amino acid concentration and the essential amino acid anion concentration, respectively. $[L]$ was calculated by equation (2.1), $[HL]$ was obtained directly from the experimental conditions and $[H]$ from the pH of the solution. $\Delta E_{\frac{1}{2}}$ was determined from the difference in $E_{\frac{1}{2}}$ of Cd(II) ion and Cd(II)-essential amino acid system. The polarograms of the systems of Cd(II)-L-leucine, Cd(II)-L-methionine, Cd(II)-L-phenylalanine, Cd(II)-L-tryptophan and Cd(II)-L-valine at various excess concentrations of the essential amino acids (in the range of 4.00×10^{-4} - 1.00×10^{-1} M) are also shown respectively in

Table 4.8 A Effects of L-isoleucine concentrations on the polarographic characteristics of Cd(II) -L-isoleucine system,
$[HL]$ = L-isoleucine concentration and
$[L]$ = L-isoleucinate anion concentration

$[HL] \times 10^2$ (M)	pH	$-\log[L]$	$-E_{1/2}$ (V vs SCE)	$\Delta E_{1/2}$ (V)	i_d (μA)	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$ (V)
0.00	7.43	-	0.689	-	2.12	0.030
0.04	7.45	5.188	0.788	0.109	1.90	0.031
0.08	7.43	4.907	0.806	0.117	1.87	0.030
0.16	7.42	4.616	0.813	0.124	1.84	0.030
0.60	7.45	4.012	0.844	0.155	1.78	0.031
2.00	7.47	3.469	0.910	0.221	1.68	0.031
4.00	7.46	3.178	0.931	0.242	1.61	0.030
10.00	7.43	2.810	0.956	0.267	1.53	0.030

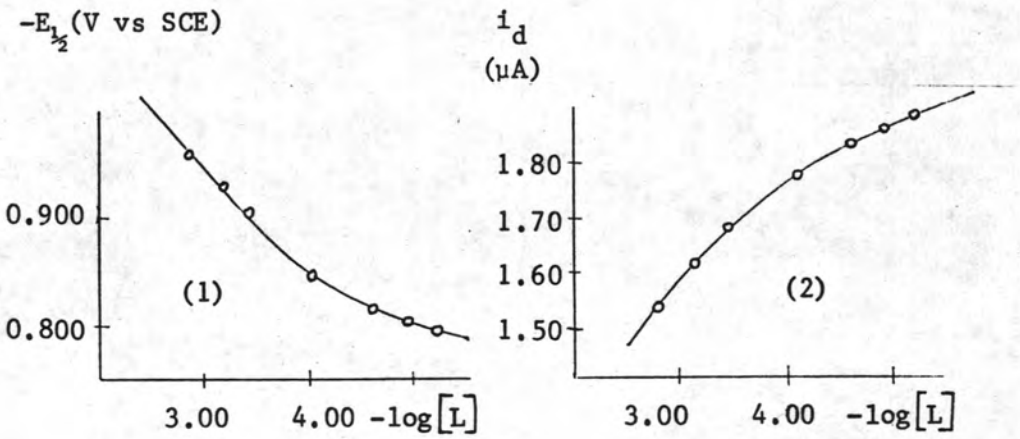

Figure 4.8 A Dependences of L-isoleucinate anion concentrations on $E_{1/2}$ (1) and i_d (2) of Cd (II) -L-isoleucine system

Table 4.8 B Effects of L-leucine concentrations on the polarographic characteristics of Cd(II)-L-leucine system, [HL] = L-leucine concentration and [L] = L-leucinate anion concentration

$[HL] \times 10^2$ (M)	pH	$-\log[L]$	$-E_{1/2}$ (V vs SCE)	$\Delta E_{1/2}$ (V)	i_d (μA)	$E_{3/4} - E_{1/4}$ (V)
0.00	7.43	-	0.689	-	2.12	0.030
0.04	7.46	5.198	0.796	0.107	1.93	0.033
0.08	7.45	4.907	0.804	0.115	1.90	0.032
0.16	7.46	4.596	0.812	0.123	1.87	0.033
0.60	7.44	4.042	0.754	0.165	1.80	0.032
2.00	7.41	3.549	0.907	0.218	1.73	0.031
4.00	7.43	3.228	0.939	0.240	1.62	0.032
10.00	7.44	2.820	0.957	0.268	1.50	0.033

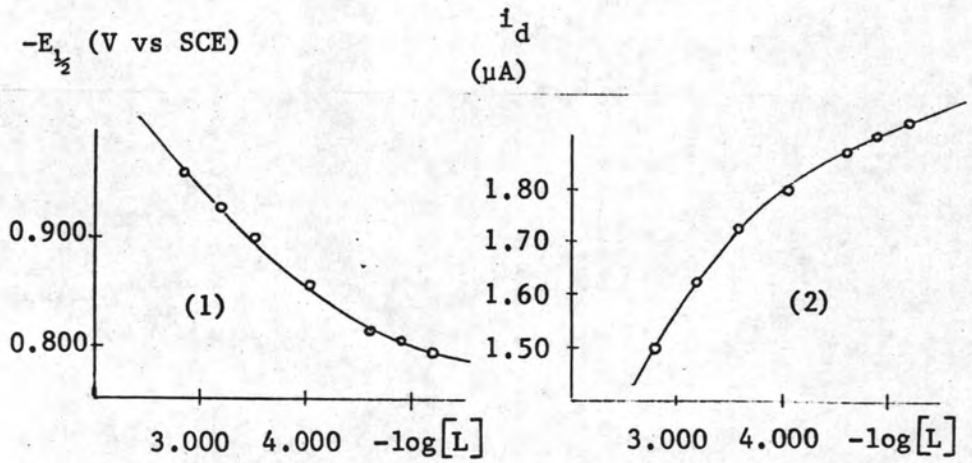

Figure 4.8 B Dependences of L-leucinate anion concentrations on $E_{1/2}$ (1) and i_d (2) of Cd(II) -L-leucine system

Table 4.8 C Effects of L-lysine concentrations on the polarographic characteristies of Cd(II) -L-lysine system,
[HL] = L-lysine concentration and
[L] = L-lysinate anion concentration

$[HL] \times 10^2$ (M)	pH	-log[L]	$-E_{1/2}$ (V vs SCE)	$\Delta E_{1/2}$ (V)	i_d (μA)	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$ (V)
0.00	7.43	-	0.689	-	2.12	0.030
0.04	7.45	4.588	0.757	0.068	1.16	0.031
0.08	7.46	4.277	0.768	0.079	1.58	0.031
0.16	7.48	3.965	0.779	0.090	1.57	0.030
0.60	7.46	3.402	0.799	0.110	1.53	0.031
2.00	7.47	2.869	0.817	0.128	1.50	0.031
4.00	7.47	2.568	0.828	0.139	1.48	0.032
10.00	7.45	2.190	0.841	0.152	1.46	0.033

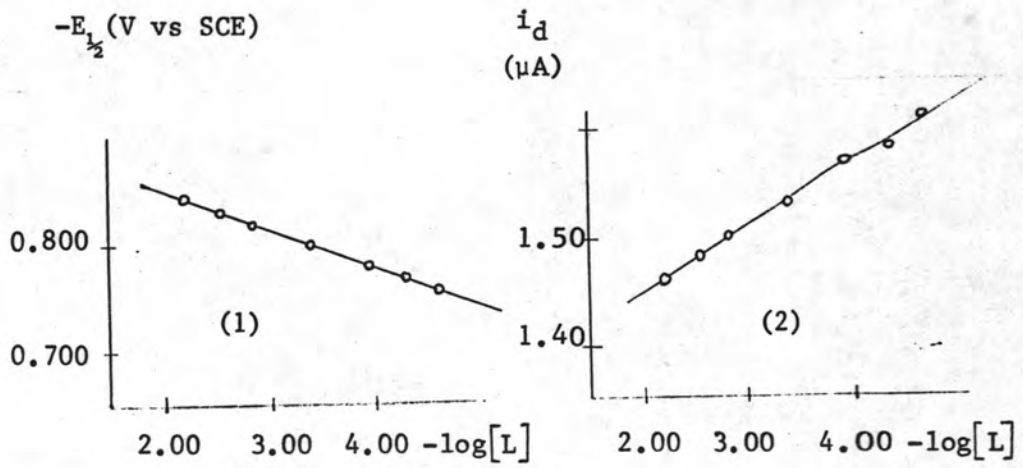

Figure 4.8 C Dependences of L-lysinate anion concentrations on $E_{1/2}$ (1) and i_d (2) of Cd(II)-L-lysine system

Table 4.8 D Effects of L-methionine concentrations on the polarographic characteristics of Cd(II) -L-methionine system,
[HL] = L-methionine concentration and
[L] = L-methionate anion concentration

$[HL] \times 10^2$ (M)	pH	$-\log[L]$	$-E_{1/2}$ (V vs SCE)	$\Delta E_{1/2}$ (V)	i_d (μA)	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$ (V)
0.00	7.43	-	0.689	-	2.12	0.030
0.04	7.44	4.718	0.824	0.135	1.81	0.030
0.08	7.47	4.387	0.832	0.143	1.80	0.031
0.16	7.45	4.106	0.838	0.149	1.78	0.031
0.60	7.44	3.542	0.869	0.180	1.76	0.031
2.00	7.47	2.989	0.927	0.238	1.72	0.032
4.00	7.46	2.689	0.948	0.259	1.69	0.032
10.00	7.44	2.320	0.975	0.286	1.62	0.032

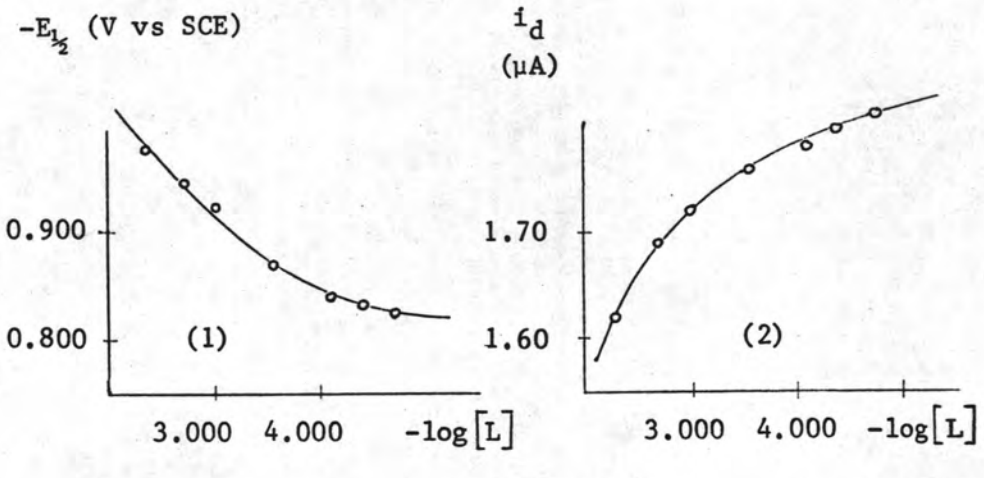

Figure 4.8 D Dependences of L-methionate anion concentrations on $E_{1/2}$ (1) and i_d (2) of Cd(II) -L-methionine system

Table 4.8 E Effects of L-phenylalanine concentrations on the polarographic characteristics of Cd(II) -L-phenylalanine system,
[HL] = L-phenylalanine concentration and
[L] = L-phenylalanate anion concentration

$[HL]\times10^2$ (M)	pH	$-\log[L]$	$-E_{1/2}$ (V vs SCE)	$\Delta E_{1/2}$ (V)	i_d (μA)	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$ (V)
0.00	7.43	-	0.689	-	2.12	0.030
0.04	7.42	4.828	0.822	0.133	1.79	0.032
0.08	7.40	4.547	0.828	0.139	1.77	0.030
0.16	7.41	4.236	0.836	0.147	1.73	0.030
0.60	7.44	3.632	0.867	0.178	1.68	0.030
2.00	7.43	3.119	0.925	0.236	1.60	0.032
4.00	7.43	2.818	0.946	0.257	1.54	0.030
10.00	7.42	2.430	0.974	0.285	1.38	0.030

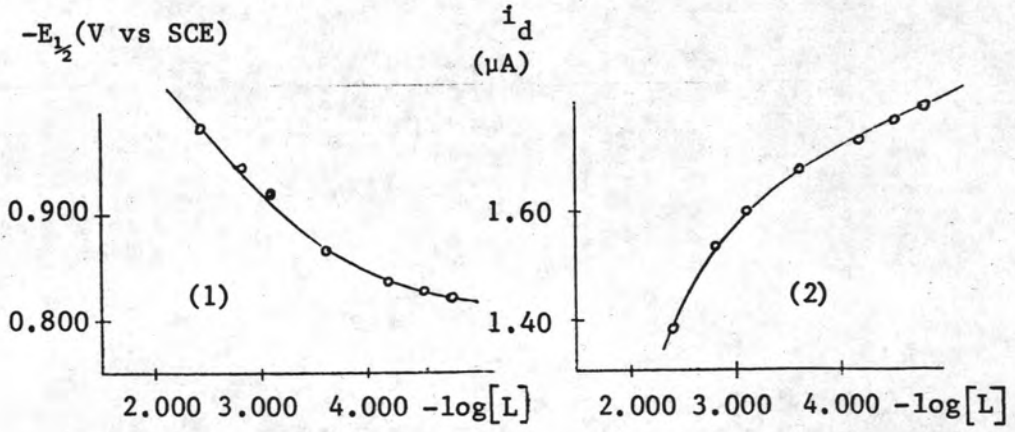

Figure 4.8 E Dependences of L-phenylalanate anion concentrations on $E_{1/2}$ (1) and i_d (2) of Cd(II) -L-phenylalanine system

Table 4.8 F Effects of L-threonine concentrations on the polarographic characteristics of Cd(II) -L-threonine system, $[HL]$ = L-threonine concentration and $[L]$ = L-threonate anion concentration

$[HL]\times10^2$ (M)	pH	$-\log[L]$	$-E_{1/2}$ (V vs SCE)	$\Delta E_{1/2}$ (V)	i_d (μA)	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$ (V)
0.00	7.43	-	0.689	-	2.12	0.030
0.04	7.41	4.658	0.830	0.141	1.63	0.031
0.08	7.49	4.277	0.839	0.150	1.62	0.030
0.16	7.42	4.046	0.845	0.156	1.61	0.031
0.60	7.48	3.412	0.887	0.198	1.59	0.030
2.00	7.45	2.919	0.939	0.250	1.58	0.031
4.00	7.48	2.588	0.962	0.273	1.55	0.031
10.00	7.46	2.210	0.989	0.300	1.51	0.031

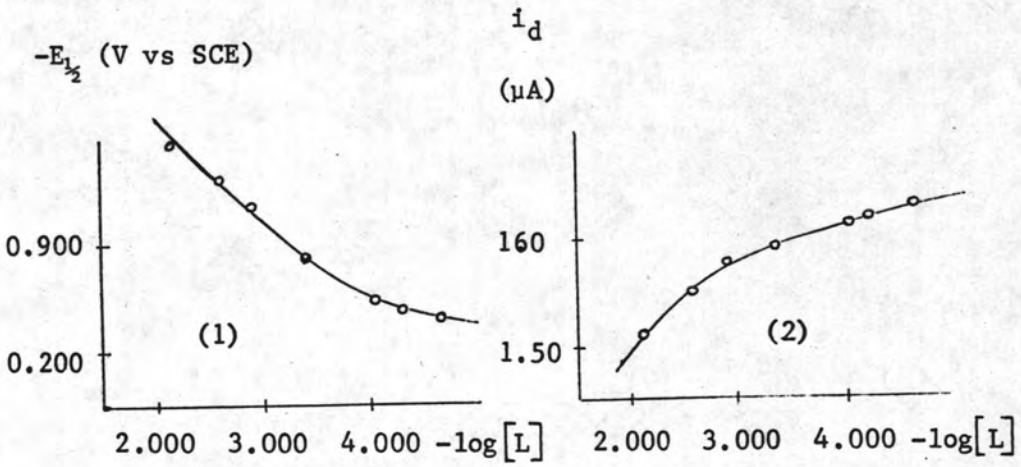

Figure 4.8 F Dependences of L-threonate anion concentrations on $E_{1/2}$ (1) and i_d (2) of Cd(II) -L-threonine system

Table 4.8 G Effects of L-tryptophan concentrations on the polarographic characteristics of Cd(II) -L-tryptophan system,
[HL] = L-tryptophan concentration and
[L] = L-tryptophanate anion concentration

$[HL] \times 10^2$ (M)	pH	$-\log[L]$	$-E_{1/2}$ (V vs SCE)	$\Delta E_{1/2}$ (V)	i_d (μA)	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$ (V)
0.00	7.43	-	0.689	-	2.12	0.030
0.04	7.43	5.168	0.838	0.149	1.89	0.030
0.08	7.45	4.847	0.844	0.155	1.88	0.030
0.16	7.42	4.576	0.850	0.161	1.87	0.031
0.60	7.44	3.982	0.874	0.185	1.85	0.031
2.00	7.46	3.439	0.928	0.239	1.82	0.031
4.00	7.48	3.118	0.950	0.261	1.80	0.030
10.00	7.43	2.770	0.974	0.285	1.76	0.030

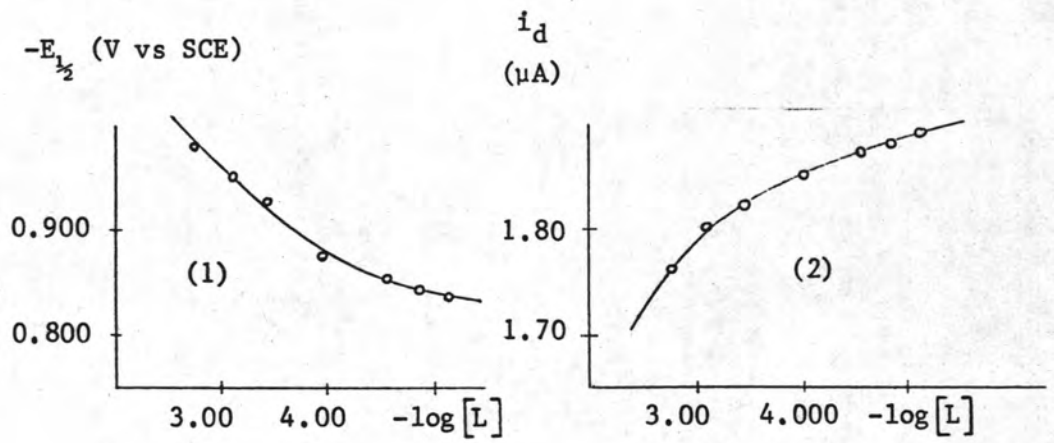

Figure 4.8 G Dependences of L-tryptophanate anion concentrations on $E_{1/2}$ (1) and i_d (2) of Cd (II) -L-tryptophan system

Table 4.8 H Effects of L-valine concentrations on the polarographic characteristics of Cd(II) -L-valine system,
[HL] = L-valine concentration and
[L] = L-valinate anion concentration

$[HL] \times 10^2$ (M)	pH	-log[L]	$E_{1/2}$ (V vs SCE)	$\Delta E_{1/2}$ (V)	i_d (μA)	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$ (V)
0.00	7.43	-	0.689	-	2.12	0.030
0.04	7.42	5.118	0.805	0.116	1.76	0.031
0.08	7.43	4.807	0.813	0.124	1.75	0.030
0.16	7.41	4.526	0.820	0.131	1.75	0.030
0.60	7.43	3.932	0.852	0.163	1.72	0.030
2.00	7.42	3.419	0.901	0.212	1.69	0.031
4.00	7.41	3.128	0.922	0.233	1.64	0.031
10.00	7.43	2.710	0.951	0.262	1.62	0.031

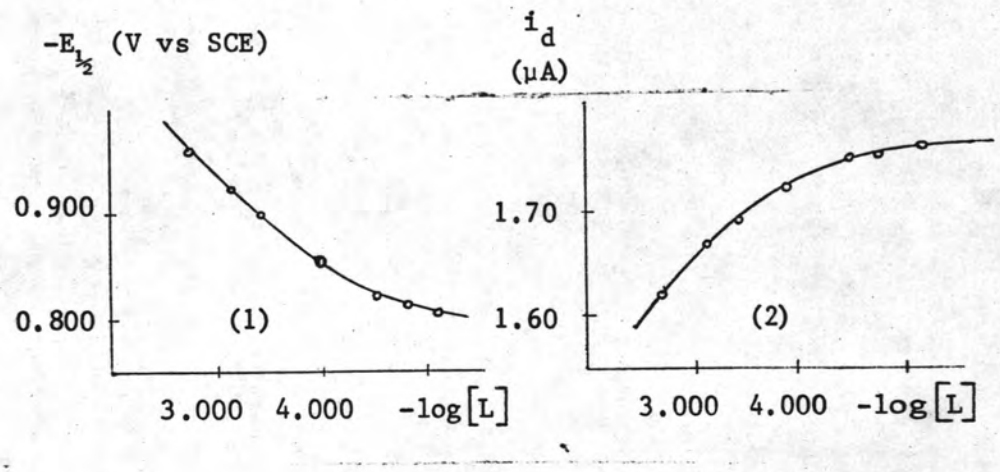

Figure 4.8 H Dependences of L-valinate anion concentrations on $E_{1/2}$ (1) and i_d (2) of Cd(II) -L-valine system

Figure 4.7 A - 4.7 E. The dependences of the essential amino acid anion concentrations on the polarographic characteristics, $E_{\frac{1}{2}}$ vs log [L] and i_d vs log [L] , were plotted as shown respectively for each system in Figure 4.8 A - 4.8 H. At pH 7.4, while the concentration of the essential amino acid anion increased, the $E_{\frac{1}{2}}$ of Cd(II)-essential amino acid systems shifted to more negative potential and the i_d decreased (see Table 4.8 A - 4.8 H and Figure 4.8 A - 4.8 H). These evidences showed that the complex formations were taken place in the solutions of each system. The values evaluated from $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ (see Table 4.8 A - 4.8 H) showed that the reductions of Cd(II) ion in the presence of these essential amino acids were reversible. The effect of the heights of Hg-reservior (h) in the range of 40.0 - 70.0 cm at pH 7.4 on i_d for each system is shown respectively in Table 4.9 A - 4.9 H and the plots of i_d vs $h^{\frac{1}{2}}$ giving linear lines passed through the origin for all systems (see Figure 4.9 A - 4.9 H) showed that these systems were diffusion-controlled. The plots of $E_{\frac{1}{2}}$ vs log [L] gave the linearity for the system of Cd(II)-L-lysine (see Figure 4.8C) thereby the formation of a single complex was indicated but gave the smooth curves for the systems of Cd(II)-L-isoleucine, Cd(II) -L-leucine, Cd(II)-L-methionine, Cd(II)-L-phenylalanine, Cd(II)-L-threonine, Cd(II)-L-tryptophan and Cd(II)-L-valine (see Figure 4.8 A - 4.8 H) thereby the successive complexes were formed. To confirm these results, the plots of $\Delta E_{\frac{1}{2}}$ vs log [L] by least squares method showed one linear portion for Cd(II)-L-lysine system (see Figure 4.10C) and showed two linear portions with the clear difference of slope for the systems of Cd(II)-L-isoleucine, Cd(II)-L-leucine, Cd(II)-L-methionine, Cd(II)-L-phenylalanine, Cd(II)-L-threonine, Cd(II)-L-

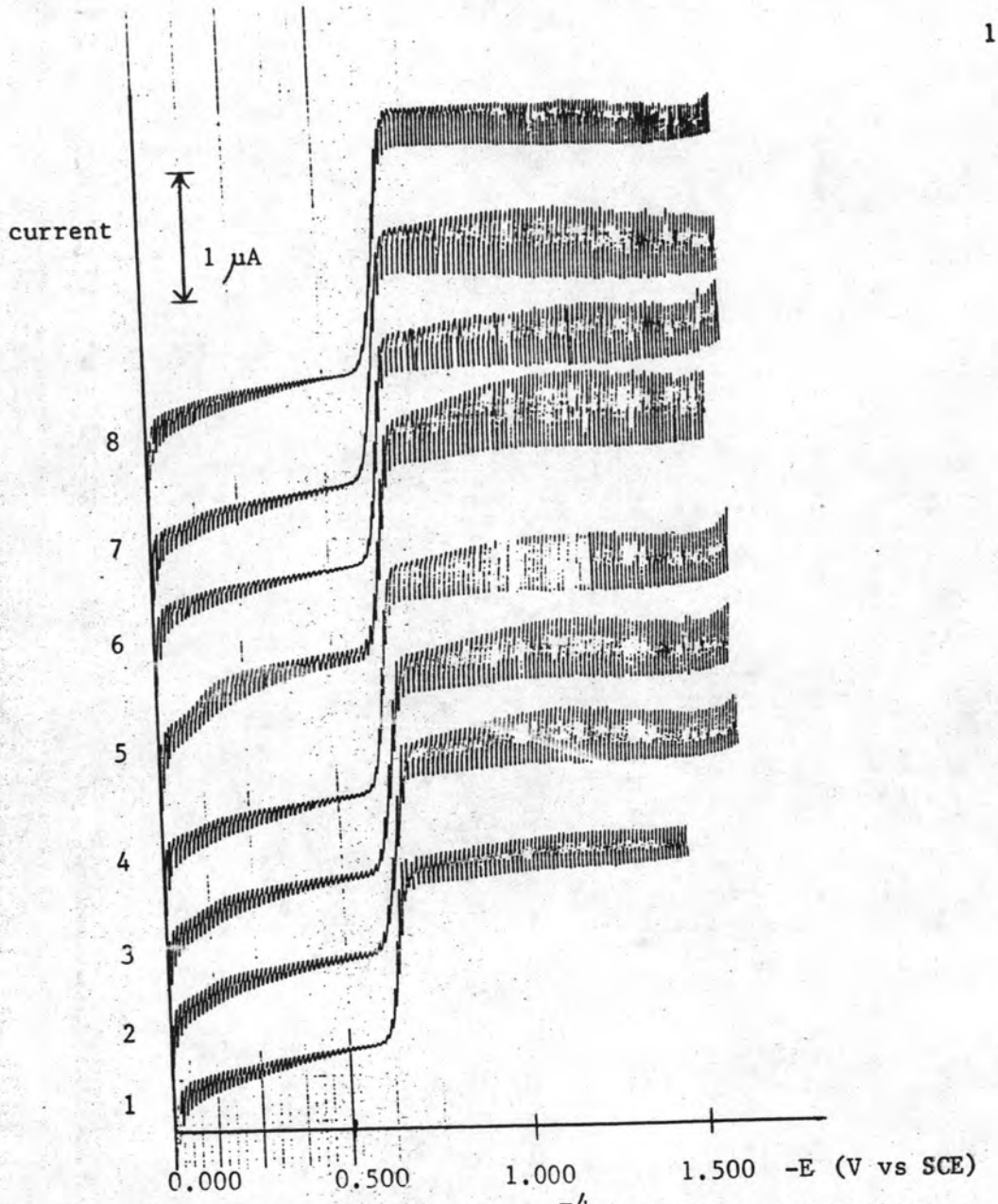

Figure 4.7 A Polarograms of 1.00×10^{-4} M Cd(II) ion and various concentrations of L-leucine in borate buffer and 0.10M KCl; 1) 1.00×10^{-1} M pH 7.44, 2) 4.00×10^{-2} M pH 7.43, 3) 2.00×10^{-2} M pH 7.41, 4) 6.00×10^{-3} M pH 7.44, 5) 1.60×10^{-3} pH 7.46, 6) 8.00×10^{-4} M pH 7.45, 7) 4.00×10^{-4} M pH 7.46 and 8) 0.00 M pH 7.43

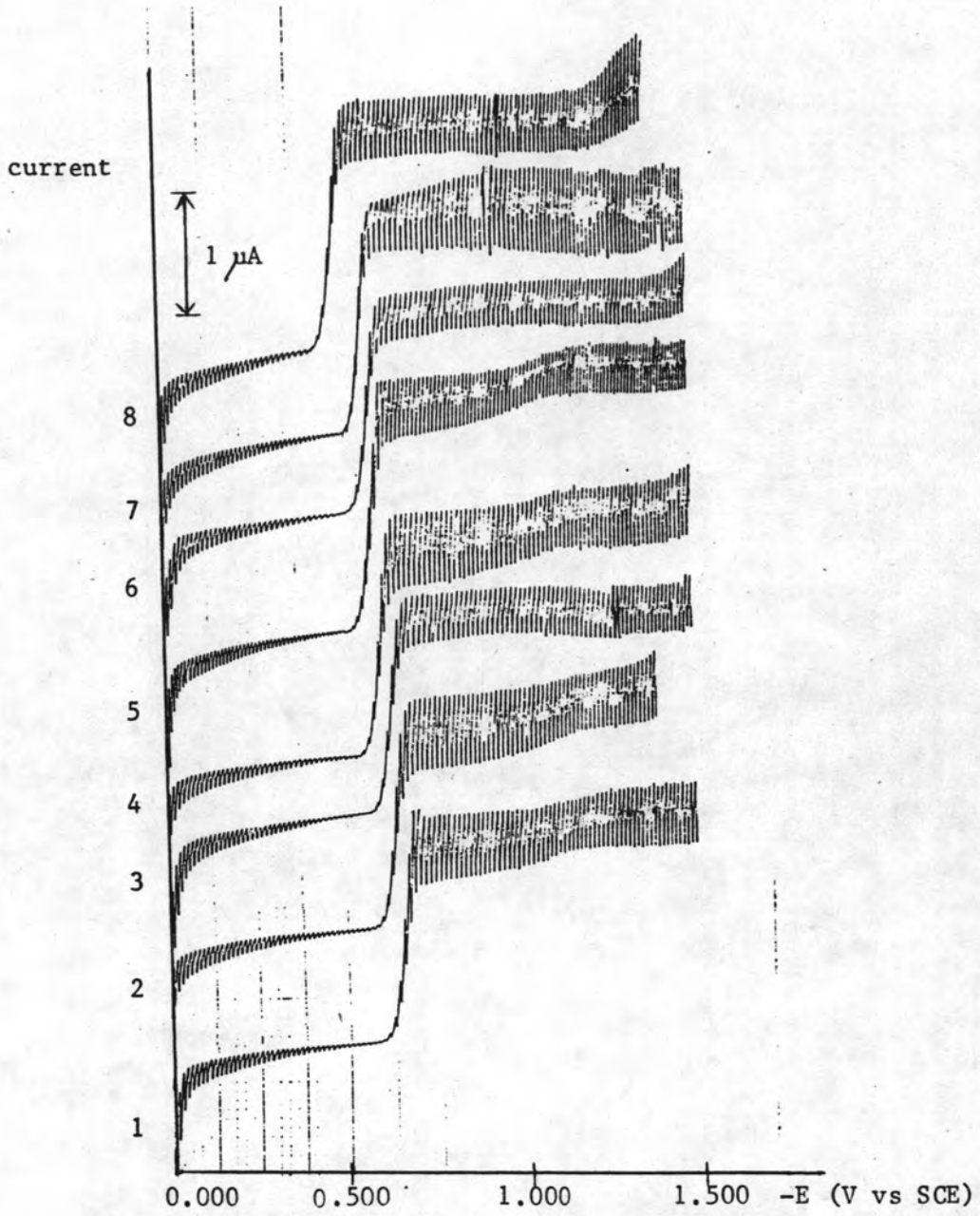

Figure 4.7 B Polarograms of 1.00×10^{-4} M Cd(II) ion and various concentrations of L-methionine in borate buffer and 0.10 M KCl; 1) 1.00×10^{-1} M pH 7.44, 2) 4.00×10^{-2} M pH 7.46, 3) 2.00×10^{-2} M pH 7.47, 4) 6.00×10^{-3} M pH 7.44 5) 1.60×10^{-3} M pH 7.45, 6) 8.00×10^{-4} M pH 7.47, 7) 4.00×10^{-4} M pH 7.44 and 8) 0.00M pH 7.43

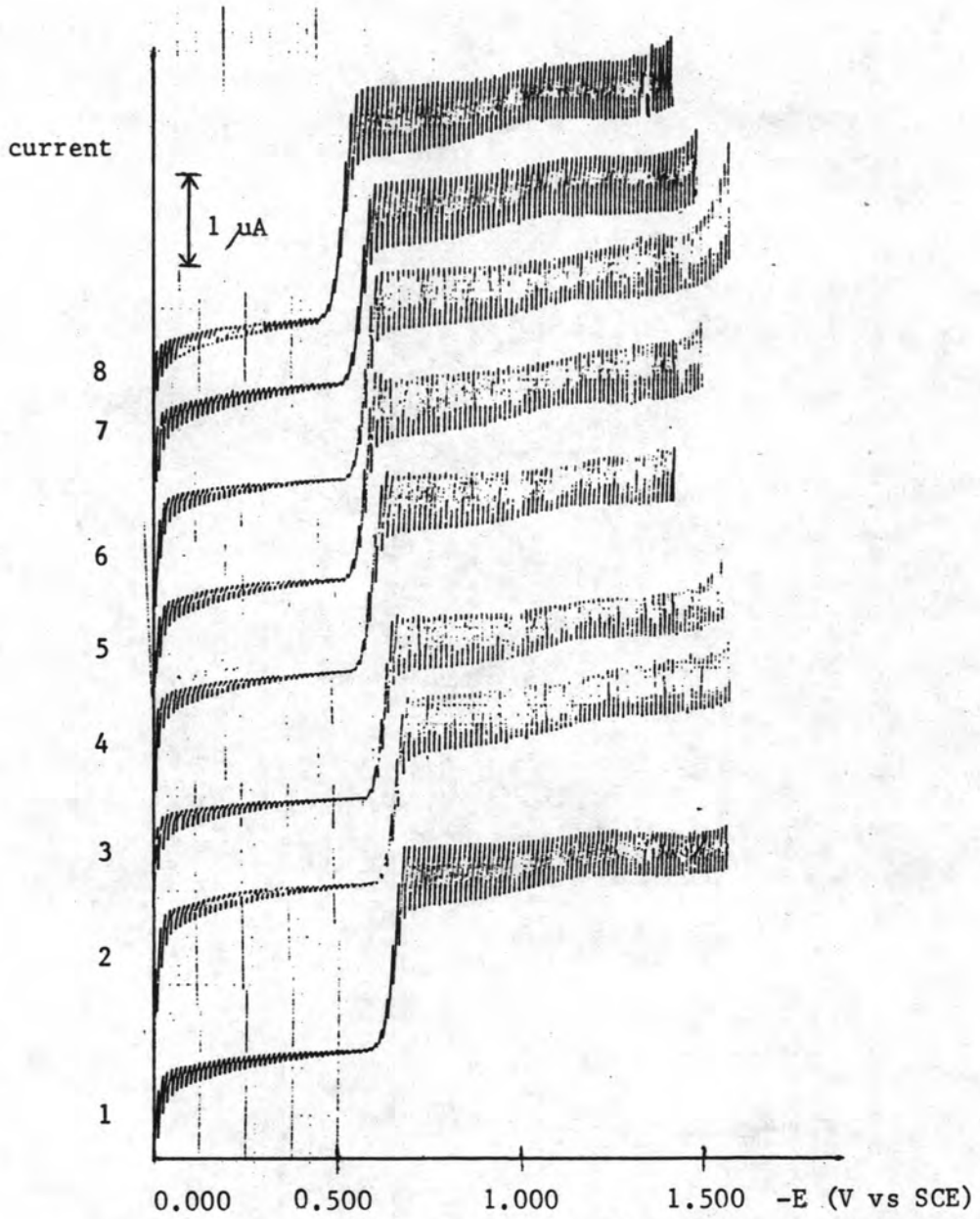

Figure 4.7 C Polarograms of 1.00×10^{-4} M Cd(II) ion and various concentrations of L-phenylalanine in borate buffer and 0.10 M KCl ; 1) 1.00×10^{-1} M pH 7.42, 2) 4.00×10^{-2} M pH 7.43, 3) 2.00×10^{-2} M pH 7.43, 4) 6.00×10^{-3} M pH 7.44 5) 1.60×10^{-3} M pH 7.41, 6) 8.00×10^{-4} M pH 7.40, 7) 4.00×10^{-4} M pH 7.42 and 8) 0.00 M pH 7.43

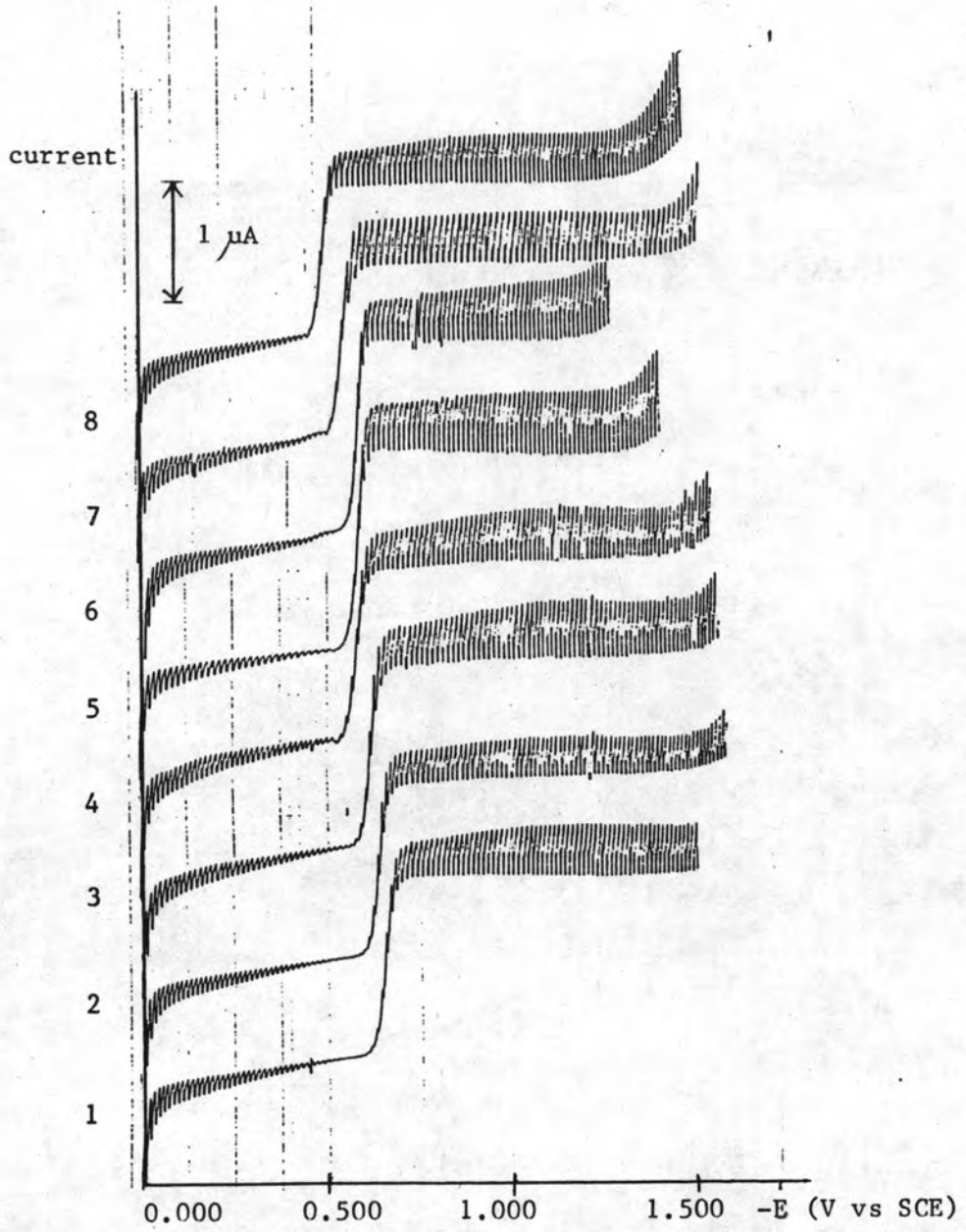

Figure 4.7 D Polarograms of 1.00×10^{-4} M Cd(II) ion and various concentrations of L-tryptophan in borate buffer and 0.10 M KCl ; 1) 1.00×10^{-1} M pH 7.43, 2) 4.00×10^{-2} M pH 7.48, 3) 2.00×10^{-2} M pH 7.46, 4) 6.00×10^{-3} M pH 7.44, 5) 1.60×10^{-3} M pH 7.42, 6) 8.00×10^{-4} M pH 7.45, 7) 4.00×10^{-4} M pH 7.43 and 8) 0.00 M pH 7.43

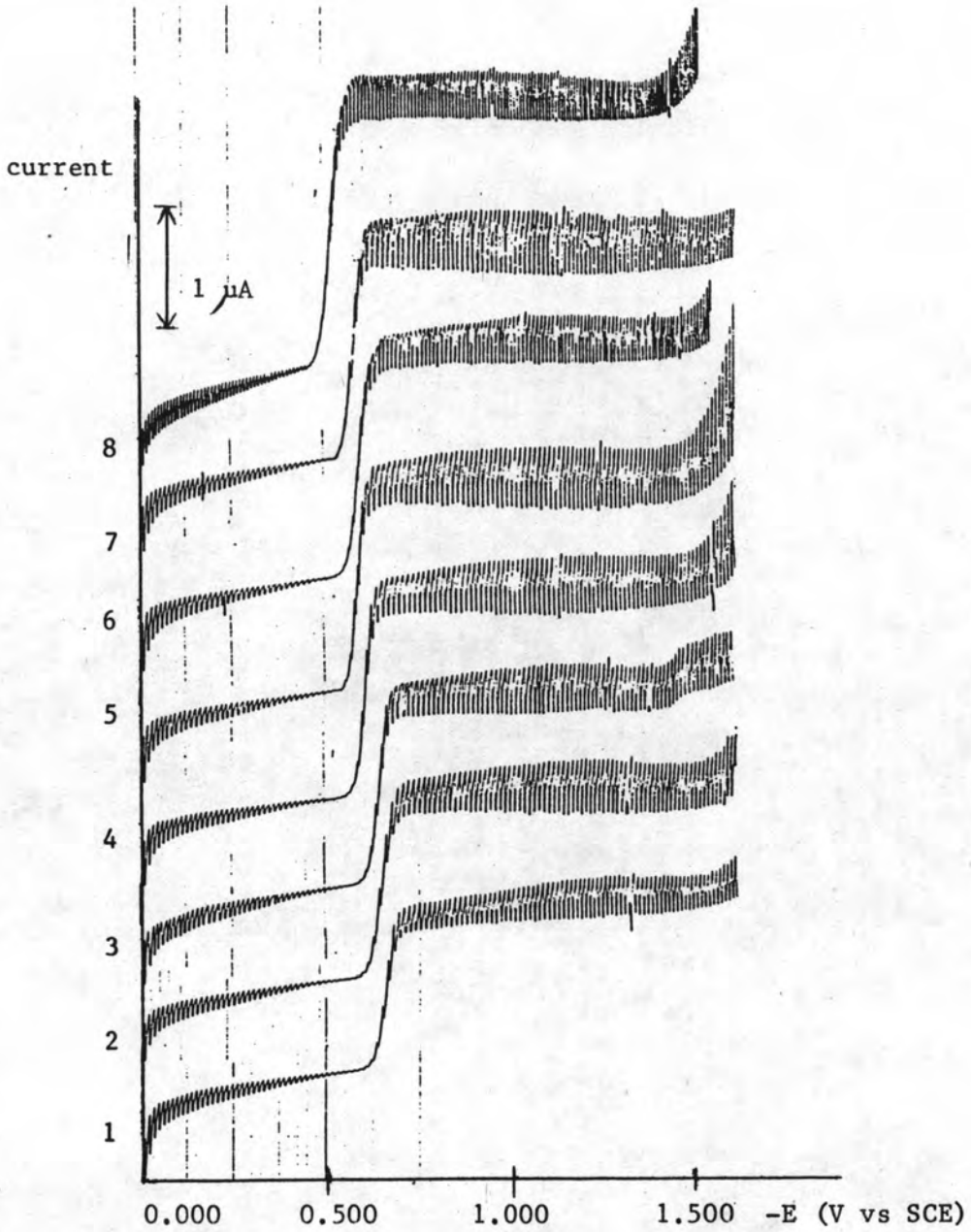

Figure 4.7 E Polarograms of 1.00×10^{-4} M Cd(II) ion and various concentrations of L-valine in borate buffer and 0.10 M KCl; 1) 1.00×10^{-1} M pH 7.43, 2) 4.00×10^{-2} M pH 7.41, 3) 2.00×10^{-2} M pH 7.42, 4) 6.00×10^{-3} M pH 7.43 , 5) 1.60×10^{-3} M pH 7.41, 6) 8.00×10^{-4} M pH 7.43, 7) 4.00×10^{-4} M pH 7.42 and 8) 0.00 M pH 7.43

Table 4.9 A Effect of h on i_d of Cd (II) -L-isoleucine system

h(cm)	$h^{1/2}(cm^{1/2})$	$i_d(\mu A)$
40.0	6.32	1.78
50.0	7.07	2.05
60.0	7.75	2.10
70.0	8.37	2.44

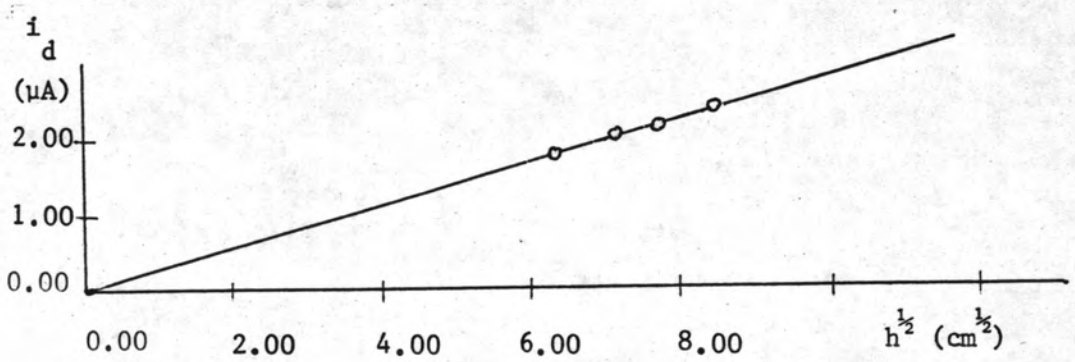

Figure 4.9 A Dependence of $h^{1/2}$ on i_d of Cd(II) -L-isoleucine system

Table 4.9 B Effect of h on i_d of Cd(II) -L-leucine system

h(cm)	$h^{1/2}(cm^{1/2})$	$i_d(\mu A)$
40.0	6.32	1.88
50.0	7.07	2.10
60.0	7.75	2.30
70.0	8.37	2.55

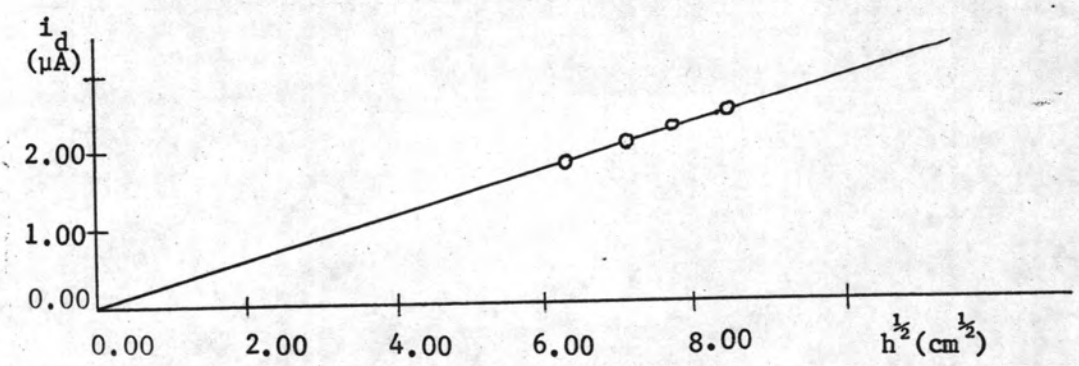

Figure 4.9 B Dependence of $h^{1/2}$ on i_d on Cd(II) -L-leucine system

Table 4.9 C Effect of h on i_d of Cd(II) -L-lysine system

h(cm)	$h^{1/2}(cm^{1/2})$	$i_d(\mu A)$
40.0	6.32	1.46
50.0	4.07	1.62
60.0	7.75	1.80
70.0	8.37	1.93

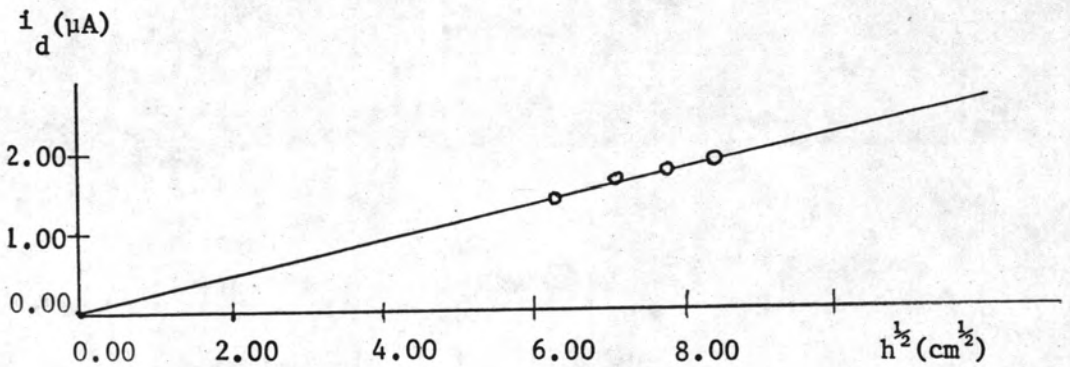

Figure 4.9 C Dependence of $h^{1/2}$ on i_d of Cd(II) -L-lysine system

Table 4.9 D Effect of h on i_d of Cd(II) -L-methionine system

h(cm)	$h^{1/2}(cm^{1/2})$	$i_d(\mu A)$
40.0	6.32	1.62
50.0	7.07	1.85
60.0	7.75	2.00
70.0	8.37	2.15

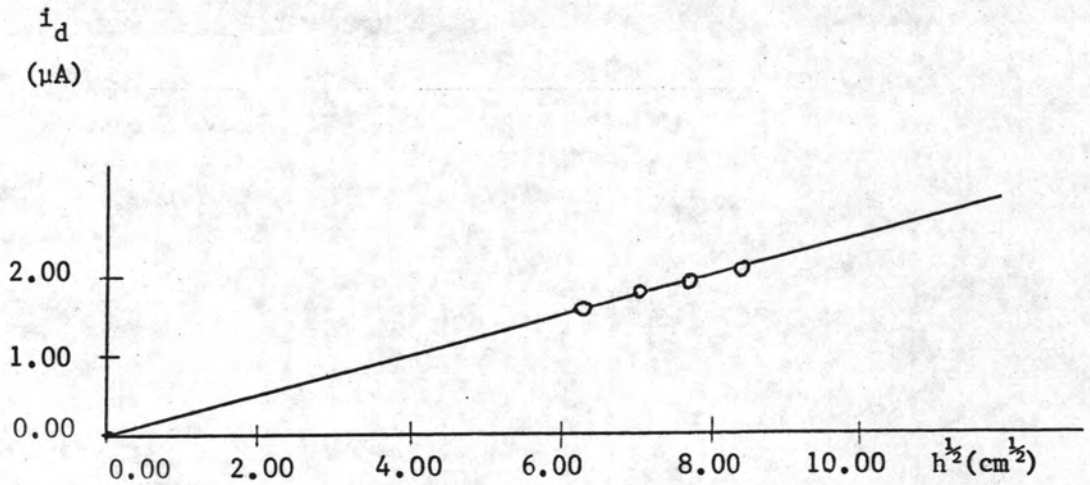

Figure 4.9 D Dependence of $h^{1/2}$ on i_d of Cd(II) -L-methionine system

Table 4.9 E Effect of h on i_d of Cd(II) -L-phenylalanine system

h(cm)	$h^{\frac{1}{2}}(cm^{\frac{1}{2}})$	$i_d(\mu A)$
40.0	6.32	1.77
50.0	7.07	2.00
60.0	7.75	2.23
70.0	8.37	2.38

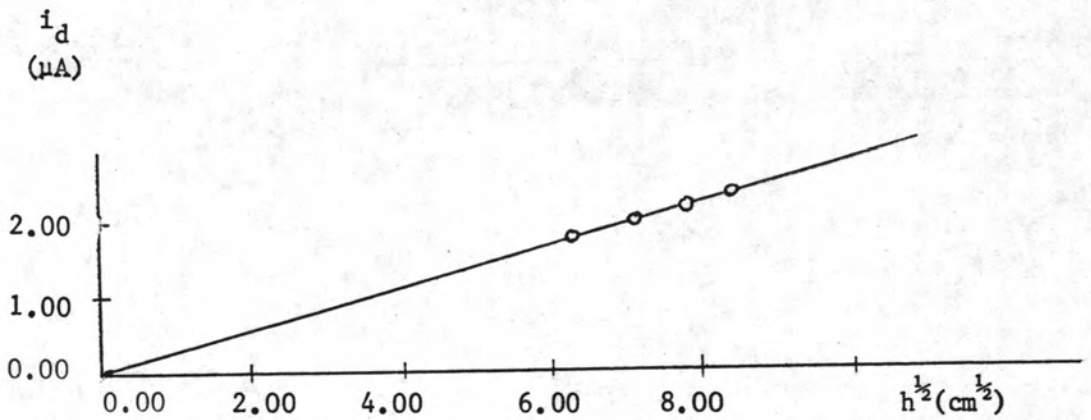

Figure 4.9 E Dependence of $h^{\frac{1}{2}}$ on i_d of Cd(II) -L- phenylalanine system

Table 4.9 F Effect of h on i_d of Cd(II) -L-threonine system

h(cm)	$h^{\frac{1}{2}}(cm^{\frac{1}{2}})$	$i_d(\mu A)$
40.0	6.32	1.51
50.0	7.07	1.85
60.0	7.75	1.90
70.0	8.37	2.10

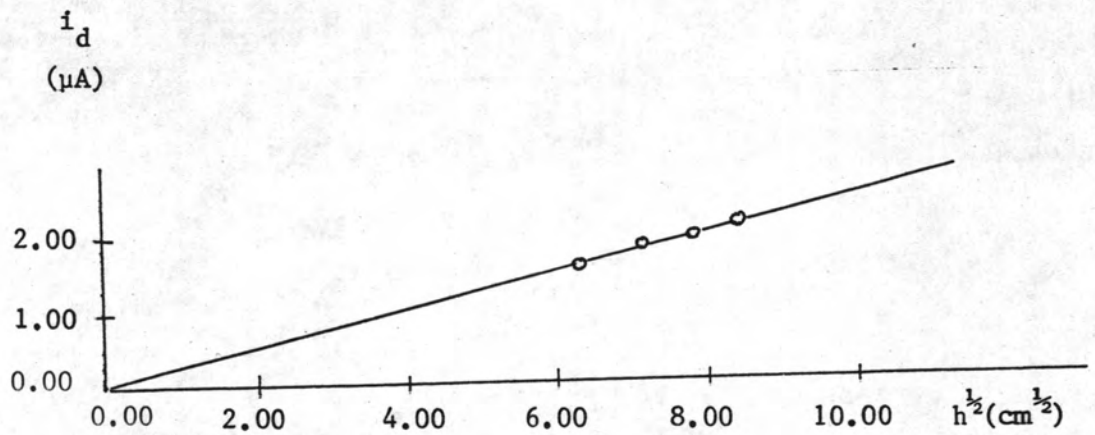

Figure 4.9 F Dependence of $h^{\frac{1}{2}}$ on i_d of Cd(II) -L- threonine system

Table 4.9 G Effect of h on i_d of Cd(II) -L-tryptophan system

h(cm)	$h^{1/2}(cm^{1/2})$	$i_d(\mu A)$
40.0	6.32	1.85
59.0	7.07	2.12
60.0	7.75	2.40
70.0	8.37	2.52

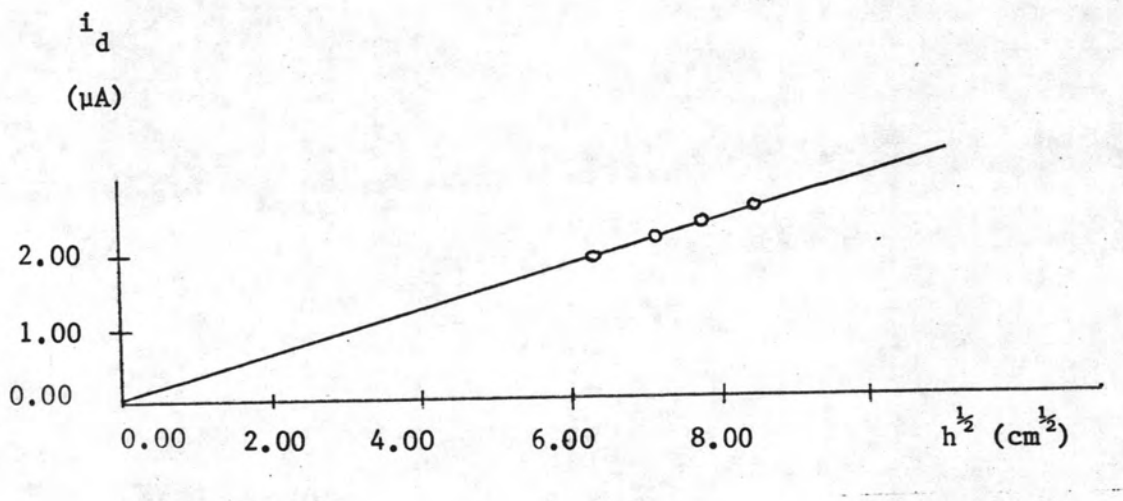

Figure 4 9 G Dependence of $h^{1/2}$ on i_d of Cd (II) -L-tryptophan system

Table 4.9 H Effect of h on i_d of Cd(II) -L-valine system

h(cm)	$h^{\frac{1}{2}}(cm^{\frac{1}{2}})$	$i_d(\mu A)$
40.0	6.32	1.62
50.0	7.07	1.81
60.0	7.75	2.07
70.0	8.37	2.20

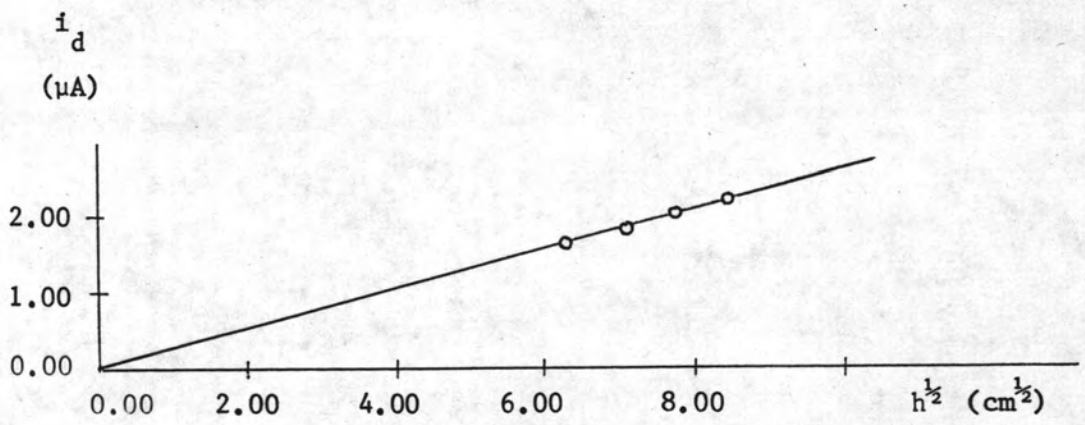

Figure 4.9 H Dependence of $h^{\frac{1}{2}}$ on i_d of Cd(II) -L-valine system

tryptophan and Cd(II)-L-valine (see Figure 4.10 A - 4.10 H). The values of coordination number (j) corresponding to the values of stability constant ($\log \beta_j$) of the complexes were interpreted from the slope and the intercept of $E_{\frac{1}{2}}$ vs $\log [L]$ plot, respectively. By equation (2.22), the value at 37°C of the slope, $j\ (2.303 \frac{RT}{nF})$, was $j\ (\frac{0.0615}{n})$ and the intercept, $(2.303 \frac{RT}{nF}) \log \beta_j$, was $(\frac{0.0615}{n}) \log \beta_j$ where n was determined by millicoulometric method of DeVries and Kroon (36) for the Cd(II), Mn(II) and Pb(II) ion in the 0.10 M KCl electrolyte solution to be 2 in each case. The values of the linear correlation coefficient (γ), the slope and the intercept of each linear portion from the plots of $\Delta E_{\frac{1}{2}}$ vs $\log [L]$ of Cd(II)-essential amino acid complexes (Figure 4.10 A - 4.10 H) including the corresponding values of j and $\log \beta_j$ were collected and tabulated as shown in Table 4.10. From Table 4.10, the values of j became 1 ($j \approx 1$) and 2 ($j \approx 2$), therefore it could be said that the composition of the Cd(II) ion to L-lysine was 1:1 and the compositions of the Cd(II) ion to L-isoleucine, Cd(II) ion to L-leucine, Cd(II) ion to L-methionine, Cd(II) ion to L-phenylalanine, Cd(II) ion to L-threonine, Cd(II) ion to L-tryptophan and Cd(II) ion to L-valine were 1:1 and 1:2 in each case.

4.4.2.2 Mn(II)-Essential Amino Acid Systems

The solutions containing 1.00×10^{-4} M Mn(II) ion in the presence of 2.00×10^{-2} M essential amino acid were studied by varying pH of the solution. The effects of pH on the polarographic characteristics of each system are shown respectively in Table 4.11 A - 4.11 H and the dependences of pH on the polarographic characteristics

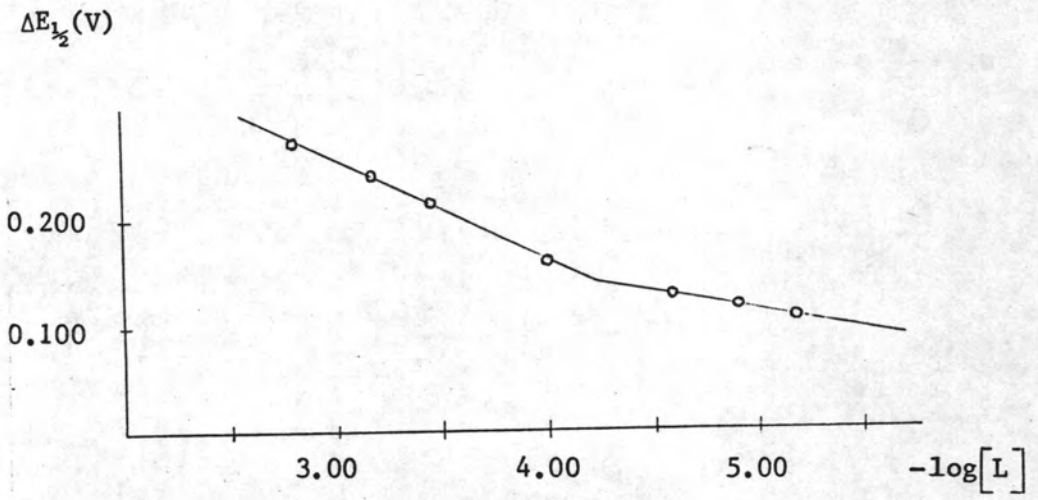

Figure 4.10 A Dependence of L-isoleucinate anion concentrations on $\Delta E_{1/2}$ of Cd(II) -L-isoleucine system

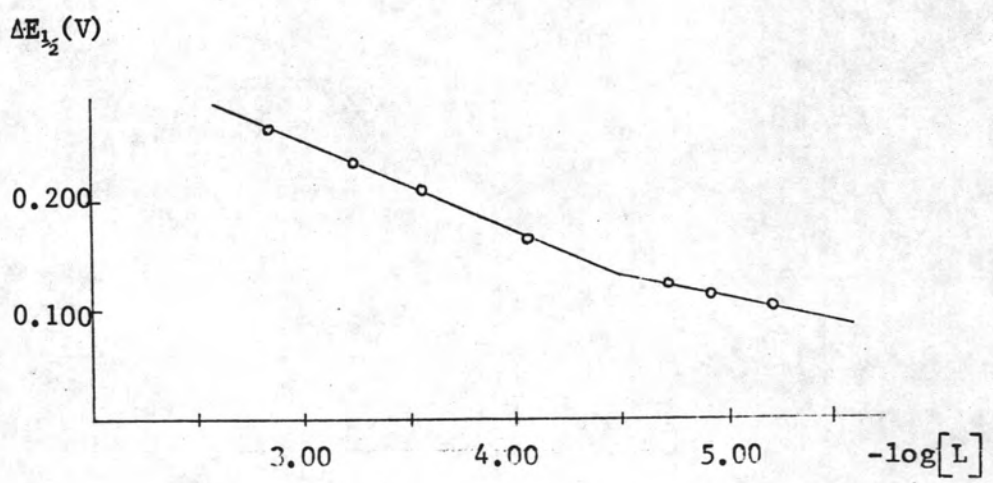

Figure 4.10 B Dependence of L-leucinate anion concentrations on $\Delta E_{1/2}$ Cd(II) -L-leucine system

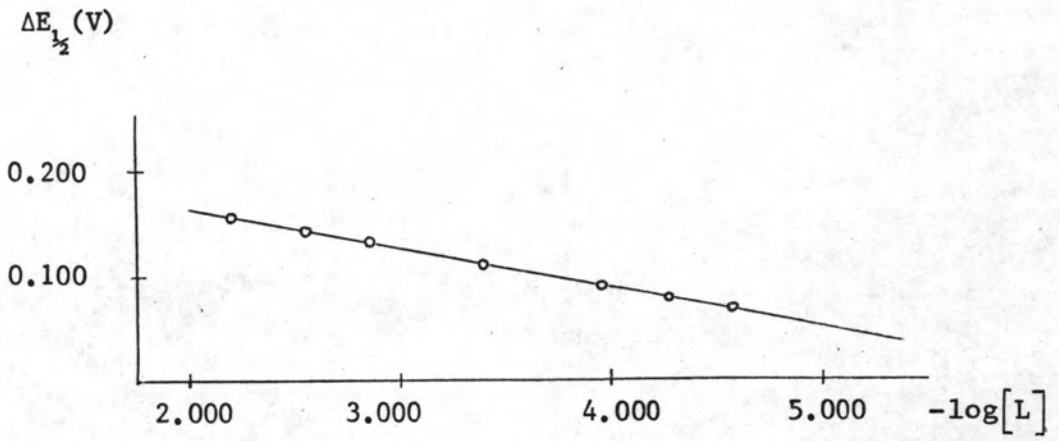

Figure 4.10 C Dependence of L-lysinate anion concentrations on $\Delta E_{1/2}$ of Cd(II) -L-lysine system

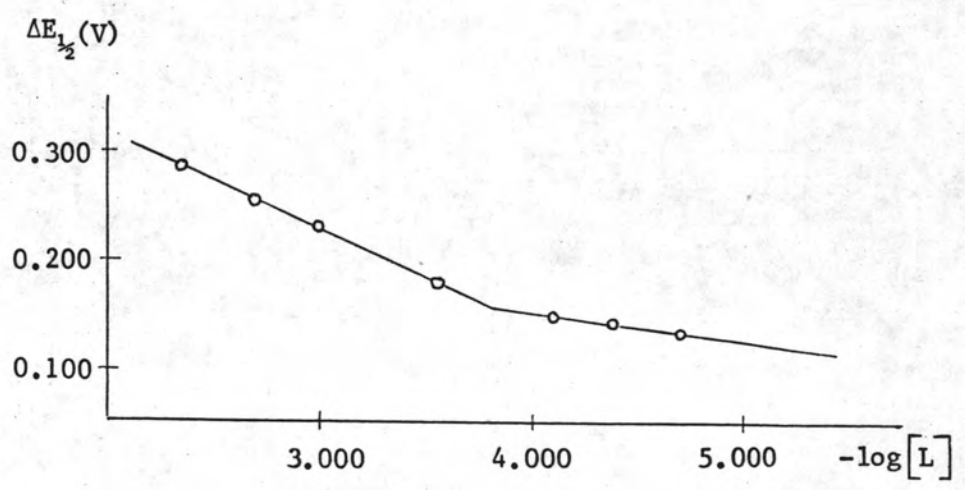

Figure 4.10 D Dependence of L-methionate anion concentrations on $\Delta E_{1/2}$ of Cd(II) -L-methionine system

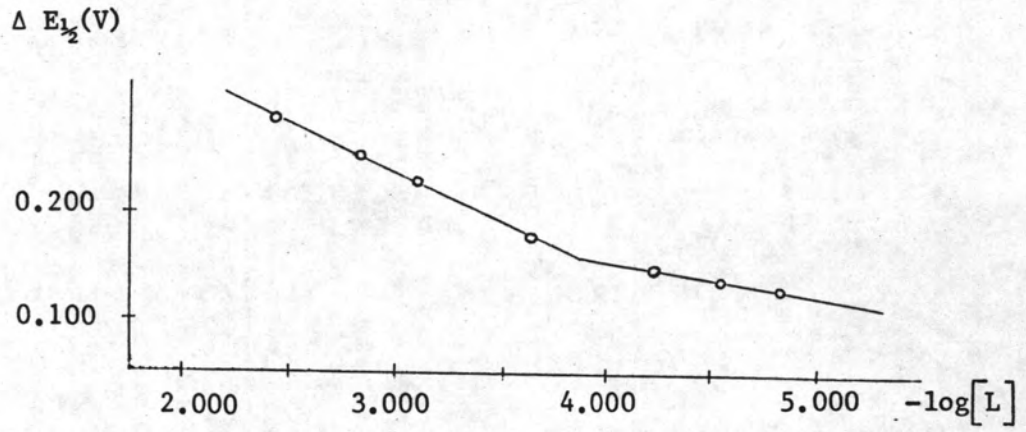

Figure 4.10 E Dependence of L-phenylalanate anion concentrations on $\Delta E_{1/2}$ of Cd(II)-L-phenylalanine system

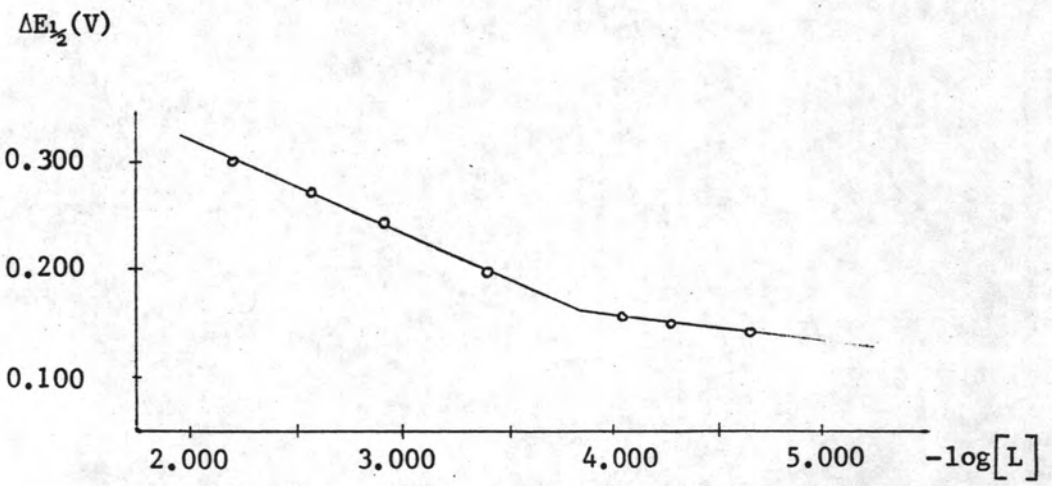

Figure 4.10 F Dependence of L-threonate anion concentrations on $\Delta E_{1/2}$ of Cd(II)-L-threonine system

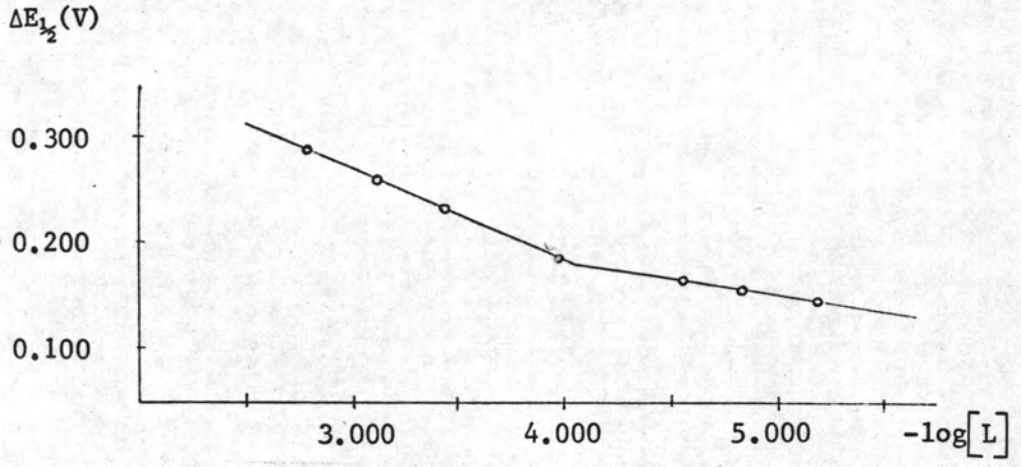

Figure 4.10 G Dependence of L-tryptophanate anion concentrations on $\Delta E_{1/2}$ of Cd(II) -L-tryptophan system

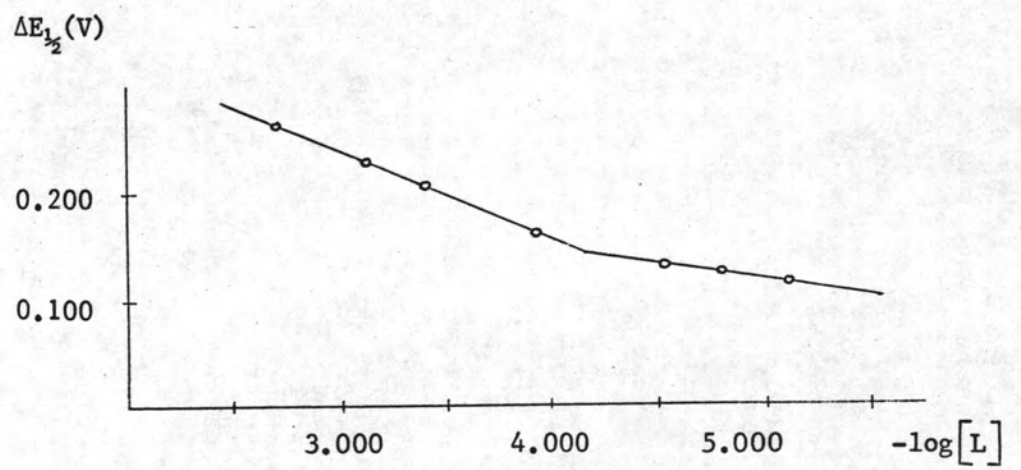

Figure 4.10 H Dependence of L-valinate anion concentrations on $\Delta E_{1/2}$ of Cd(II) -L-valine system

Table 4.10 Obtained values from each linear portion of the plot of $\Delta E_{\frac{1}{2}}$ vs $\log[L]$ from Cd(II)-essential amino acid complexes by polarographic technique

anion of Cd complex	First Linear Portion					Second Linear Portion				
	γ	slope	j	inter-cept	log β_j	γ	slope	j	inter-cept	log β_j
L-isoleucine	0.998	0.027	0.88	0.243	7.90	0.999	0.069	2.24	0.463	15.05
L-leucine	0.999	0.027	0.88	0.245	7.97	0.999	0.068	2.21	0.461	14.99
L-lysine	0.999	0.035	1.14	0.229	7.45	-	-	-	-	-
L-methionine	0.999	0.023	0.75	0.243	7.90	0.998	0.071	2.30	0.452	14.70
L-phenylala-nine	0.998	0.024	0.78	0.247	8.03	0.999	0.071	2.30	0.457	14.86
L-threonine	0.999	0.024	0.78	0.254	8.26	0.999	0.070	2.27	0.455	14.79
L-tryptophan	0.998	0.020	0.65	0.253	8.23	0.999	0.068	2.21	0.475	15.45
L-valine	0.999	0.025	0.81	0.245	7.79	0.999	0.070	2.27	0.460	14.96

Table 4.11 A Effects of pH on the polarographic characteristics of Mn(II) -L-isoleucine system

pH	$-E_{1/2}$ (V vs SCE)	i_d (μA)	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$ (V)
3.93	no wave	-	-
5.05	1.566	1.54	0.030
6.11	1.567	1.52	0.030
7.15	1.568	1.49	0.030
8.53	1.570	1.48	0.031
9.47	1.585	1.26	0.045

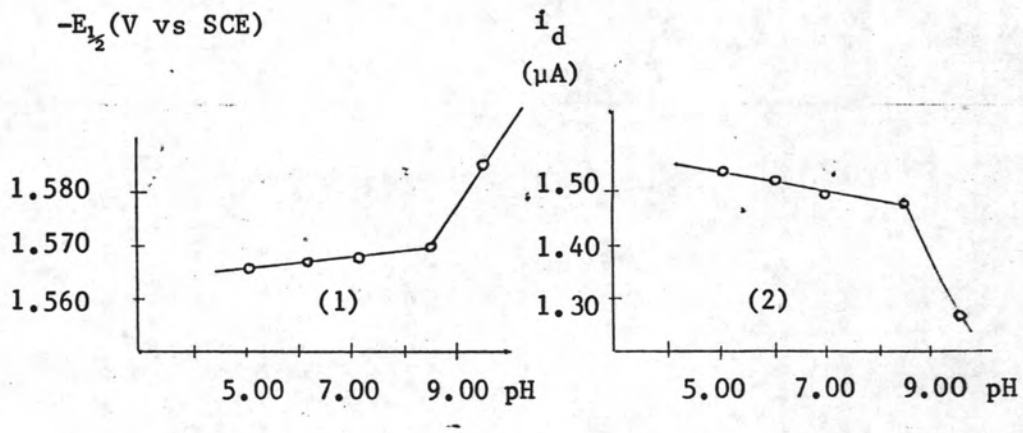

Figure 4.11 A Dependences of pH on $E_{1/2}$ (1) and i_d (2) of Mn(II) -L-isoleucine system

Table 4.11 B Effects of pH on the polarographic characteristics of Mn(II) -L-leucine sustem

pH	$-E_{1/2}$ (V vs SCE)	i_d (μA)	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$ (V)
2.74	no wave	-	-
4.01	no wave	-	-
4.92	1.566	1.65	0.030
5.89	1.565	1.62	0.030
6.75	1.568	1.60	0.030
7.51	1.569	1.59	0.030
8.03	1.570	1.58	0.031
8.54	1.572	1.58	0.031
9.03	1.591	1.47	0.048

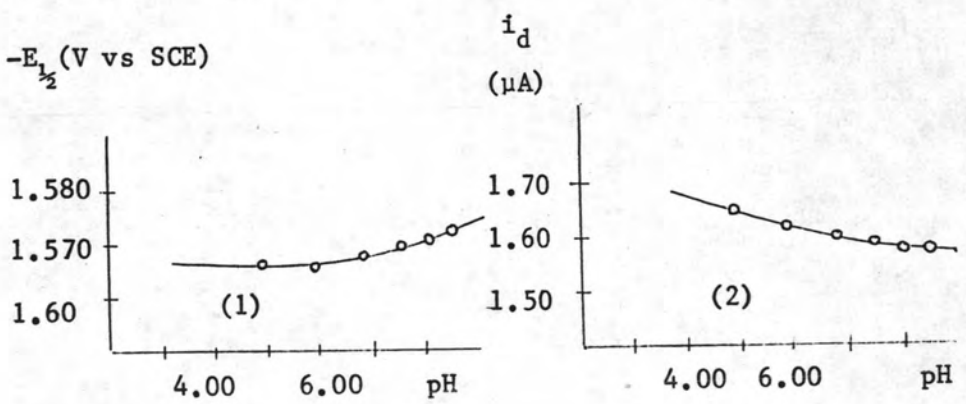

Figure 4.11 B Dependences of pH on $E_{1/2}$ (1) and i_d (2) of Mn (II) -L-leucine system

Table 4.11 C Effects of pH on the polarographic characteristics of Mn(II) -L-lysine system

pH	$-E_{\frac{1}{2}}$ (V vs SCE)	i_d (A)	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$ (V)
3.02	no wave	-	-
4.10	ill-defined wave	-	-
5.00	ill-defined wave	-	-
6.12	1.570	a	0.058
7.07	1.571	a	0.056
8.02	1.572	a	0.060
9.02	ill-defined wave	-	-

[a] can not be measured accurately because of the ill-defined wave

Table 4.11 D Effects of pH on the polarographic characteristics of Mn(II) -L-methionine system

pH	$-E_{1/2}$ (V vs SCE)	i_d (μA)	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$ (V)
3.00	no wave	-	-
4.02	no wave	-	-
5.03	1.565	1.80	0.038
5.75	1.567	1.79	0.032
6.02	1.567	1.78	0.031
6.98	1.568	1.76	0.030
7.48	1.570	1.74	0.030
8.03	1.573	1.70	0.031
8.50	1.575	1.65	0.031
9.40	1.585	0.57	0.039

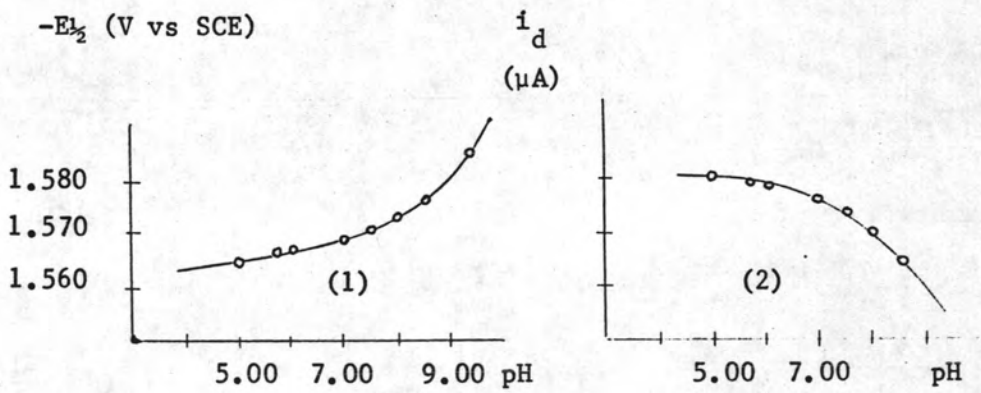

Figure 4.11 D Dependences of pH on $E_{1/2}$ (1) and i_d (2) of Mn (II) -L-methionine system

Table 4.11 E Effects of pH on the polarographic characteristics of Mn(II) -L-phenylala ine system

pH	$-E_{1/2}$ (V vs SCE)	i_d (μA)	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$ (V)
3.95	no wave	-	-
4.92	1.569	2.37	0.040
5.91	1.571	1.77	0.031
6.15	1.571	1.76	0.031
6.99	1.572	1.73	0.031
7.48	1.573	1.68	0.030
7.97	1.575	1.63	0.030
8.45	1.576	1.59	0.030
8.90	1.579	1.41	0.031
9.45	1.583	1.31	0.030
9.94	1.587	1.02	0.029

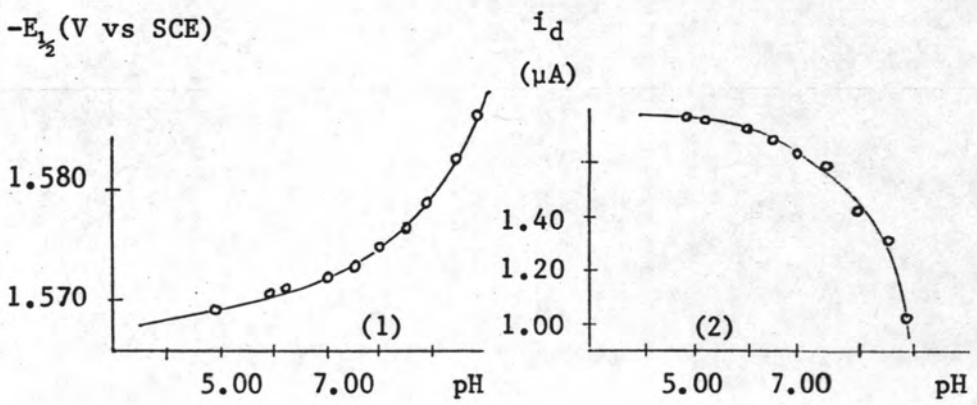

Figure 4.11 E Dependences of pH on $E_{1/2}$(1) and i_d (2) of Mn -L-phenylalanine system

Table 4.11 F Effects of pH on the polarographic characteristics of Mn(II) -L-threonine system

pH	$-E_{1/2}$ (V vs SCE)	i_d (μA)	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$ (V)
4.53	1.565	1.44	0.029
5.80	1.567	1.43	0.030
7.00	1.570	1.36	0.030
8.04	1.576	1.33	0.030
8.50	1.579	1.30	0.031
8.91	1.583	1.28	0.031

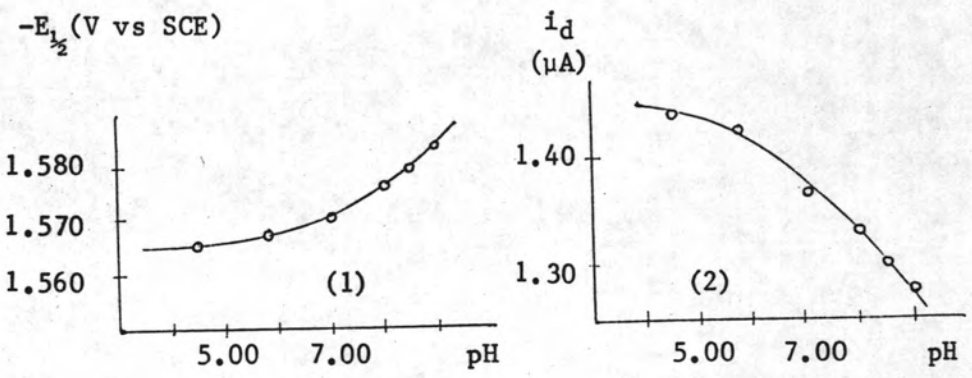

Figure 4.11 F Dependences of pH on $E_{1/2}$ (1) and i_d (2) of Mn (II) -L-threonine system

Table 4.11 G Effects of pH on the polarographic characteristics of Mn(II) -L-tryptophan system

pH	$-E_{1/2}$ (V vs SCE)	i_d (μA)	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$ (V)
4.07	no wave	-	-
6.28	1.567	1.49	0.030
7.04	1.569	1.47	0.030
7.76	1.571	1.44	0.029
8.42	1.573	1.42	0.031

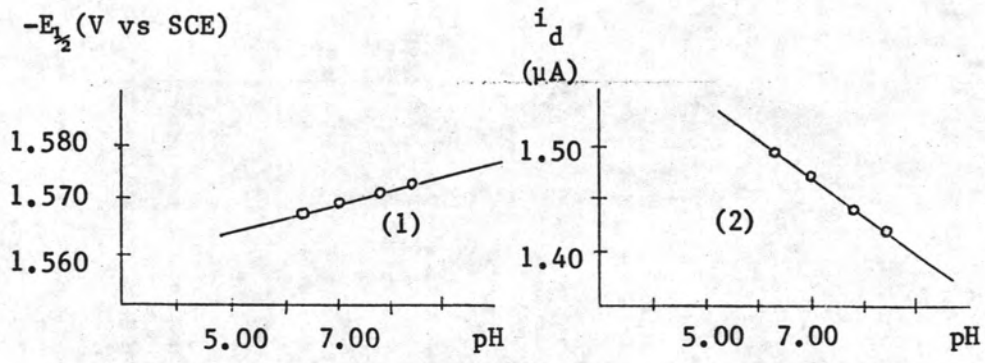

Figure 4.11 G Dependences of pH on $E_{1/2}$ (1) and i_d (2) of Mn (II) -L-tryptophan system

Table 4.11 H Effects of pH on the polarographic characteristics of Mn(II) -L-valine system

pH	$-E_{1/2}$ (V vs SCE)	i_d (μA)	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$ (V)
2.42	no wave	-	-
3.92	no wave	-	-
5.03	1.565	1.45	0.031
6.04	1.566	1.43	0.029
7.01	1.566	1.42	0.030
7.43	1.566	1.41	0.030
8.45	1.568	1.39	0.031
8.98	1.570	1.23	0.033

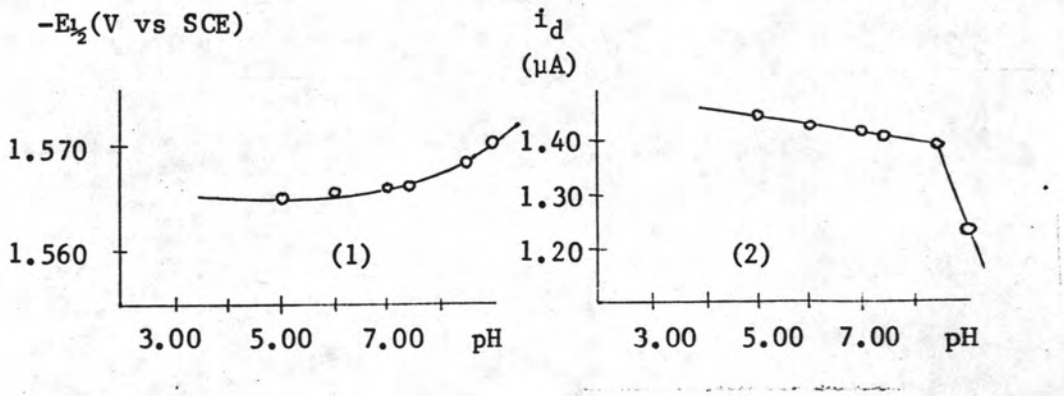

Figure 4.11 H Dependences of pH on $E_{1/2}$ (1) and i_d (2) of Mn(II) -L-valine system

were plotted as shown respectively for each system in Figure 4.11 A - 4.11 H. Exceptionally, the polarographic characteristics of Mn(II)-L-lysine system were not measured because of the ill-defined wave in all cases of this system (see Table 4.11 C). Therefore, the complex formation studies of the Mn(II)-L-lysine system can not be determined here by polarographic method. As pH increased, the i_d decreased but the increasing of negative shift in $E_{\frac{1}{2}}$ was not much and its shifting was clearly observed at above pH 8.0 for all systems (see Table 4.11 A - 4.11 H and Figure 4.11 A - 4.11 H). The electrode reaction evaluated from $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ showed the reductions of all systems were reversible in the range of pH 5-9, but they became irreversible at pH above 9.0 (see Table 4.11 A - 4.11 H). Hence, the pH 8.5 was chosen to study the complex formation of the Mn(II)-essential amino acid systems. At the constant pH, pH 8.5, the solutions containing 1.00×10^{-4} M Mn(II) ion in the presence of essential amino acid were studied by varying the essential amino acid concentrations in the range of $2.00 \times 10^{-2} - 8.00 \times 10^{-2}$ M. The effects of the essential amino acid concentrations on the polarographic characteristics of each system are shown respectively in Table 4.12 A - 4.12 H. The polarograms of the systems of Mn(II)-L-isoleucine, Mn(II)-L-leucine, Mn(II)-L-methionine, Mn(II)-L-phenylalanine, Mn(II)-L-tryptophan and Mn(II)-L-valine at various excess concentrations of the essential amino acids (in the range of $2.00 \times 10^{-2} - 8.00 \times 10^{-2}$ M) are also shown respectively in Figure 4.12 A - 4.12 F. The dependences of the essential amino acid anion concentrations on the polarographic characteristics were plotted as shown respectively for each system in Figure 4.13 A - 4.13 H. At pH 8.5, while the concentration of

Table 4.12 A Effects of L-isoleucine concentrations on the polarographic characteristics of Mn(II) -L-isoleucine system, $[HL]$ = L-isoleucine concentration and $[L]$ = L-isoleucinate anion concentration

$[HL] \times 10^2$ (M)	pH	$-\log[L]$	$-E_{1/2}$ (V vs SCE)	$\Delta E_{1/2}$ (V)	i_d (μA)	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$ (V)
0.00	8.53	-	1.565	-	1.81	0.029
2.00	8.53	2.409	1.570	0.005	1.48	0.030
3.00	8.51	2.253	1.576	0.011	1.46	0.029
4.00	8.48	2.158	1.580	0.015	1.45	0.030
5.00	8.52	2.021	1.586	0.021	1.43	0.031
6.00	8.50	1.962	1.588	9.023	1.43	0.030
7.00	8.48	1.915	1.590	0.025	1.40	0.031
8.00	8.53	1.807	1.595	0.030	1.40	0.031

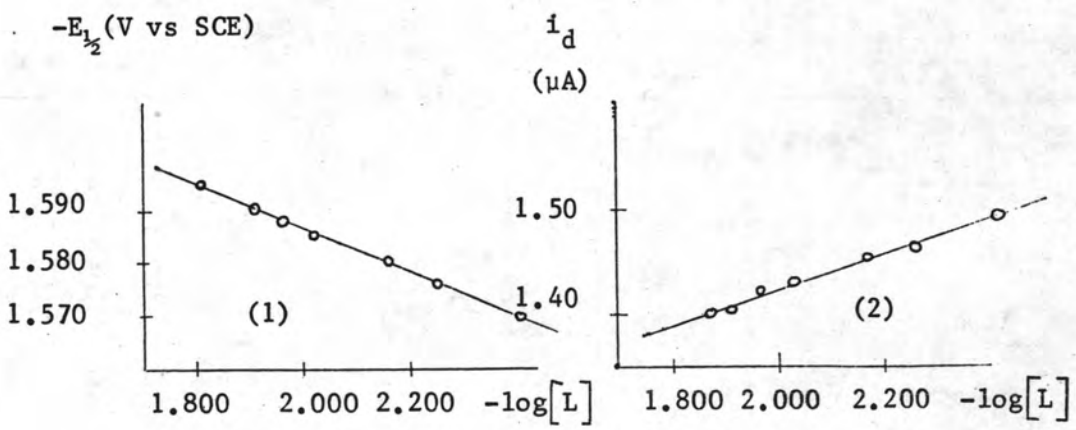

Figure 4.13 A Dependences of L-isoleucinate anion concentrations on $E_{1/2}$ (1) and i_d (2) of Mn (II) -L-isoleucine system

Table 4.12 B Effects of L-leucine concentrations on the polarographic characteristics of Mn(II) -L-leucine system, [HL] = L-leucine concentration and [L] = L-leucinate anion concentration

$[HL]\times10^2$ (M)	pH	$-\log[L]$	$-E_{1/2}$ (V vs SCE)	$\Delta E_{1/2}$ (V)	i_d (μA)	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$ (V)
0.00	8.53	-	1.565	-	1.81	0.029
2.00	8.54	2.419	1.572	0.007	1.58	0.031
3.00	8.54	2.243	1.579	0.014	1.56	0.030
4.00	8.52	2.138	1.584	0.019	1.53	0.031
5.00	8.51	2.051	1.588	0.023	1.52	0.030
6.00	8.51	1.972	1.591	0.026	1.51	0.031
7.00	8.51	1.905	1.594	0.029	1.48	0.032
8.00	8.52	1.837	1.597	0.032	1.47	0.032

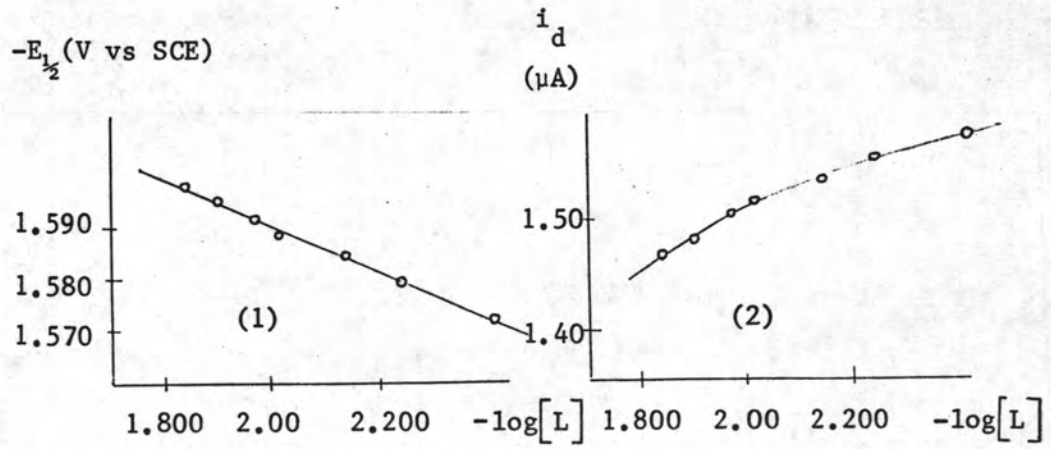

Figure 4.13 B Dependences of L-leucinate anion concentrations on $E_{1/2}$ (1) and i_d (2) of Mn(II) -L-leucine system

Table 4.12 D Effects of L-mehtionine concentrations on the polarographic characteristics of Mn(II) -L-methionine system, [HL] = L-methionine concentration and [L] = L-methionate anion concentration

$[HL]\times10^2$ (M)	pH	$-\log[L]$	$-E_{1/2}$ (V vs SCE)	$\Delta E_{1/2}$ (V)	i_d (μA)	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$ (V)
0.00	8.53	-	1.565	-	1.81	0.029
2.00	8.58	2.979	1.570	0.005	1.74	0.030
3.00	8.57	2.813	1.575	0.010	1.74	0.029
4.00	8.54	2.718	1.578	0.013	1.72	0.030
5.00	8.57	2.591	1.582	0.017	1.71	0.030
6.00	8.56	2.522	1.584	0.019	1.70	0.031
7.00	8.55	2.465	1.586	0.021	1.69	0.031
8.00	8.54	2.417	1.588	0.023	1.69	0.031

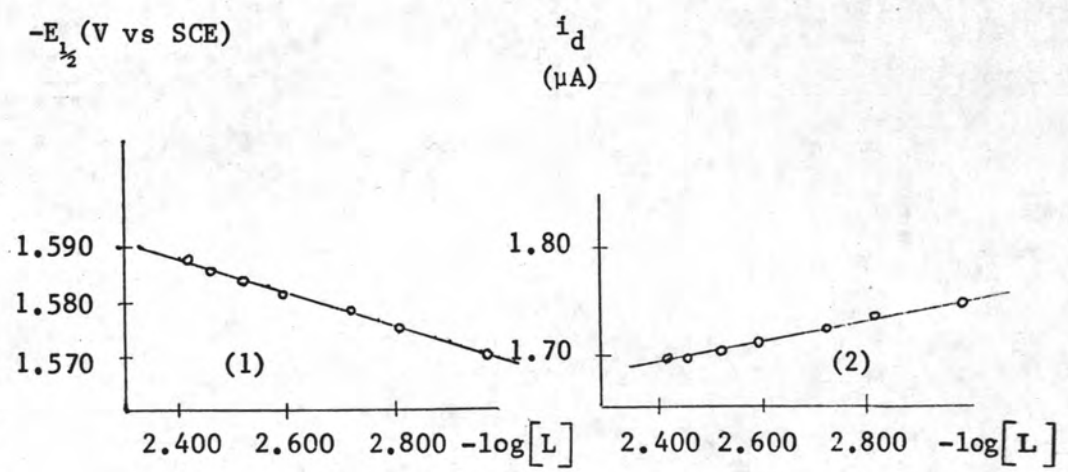

Figure 4.13 D Dependences of L-methionate anion concentrations on $E_{1/2}$ (1) and i_d (2) of Mn(II) -L-methionine system

Table 4.12 E Effects of L-phenylalanine concentrations on the polarographic characteristics of Mn(II) -L-phenylalanine system,

[HL] = L-phenylalanine concentration and

[L] = L-phenylalanate anion concentration

$[HL] \times 10^2$ (M)	pH	$-\log[L]$	$-E_{1/2}$ (V vs SCE)	$\Delta E_{1/2}$ (V)	i_d (μA)	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$ (V)
0.00	8.53	-	1.565	-	1.81	0.029
2.00	8.45	2.099	1.576	0.011	1.59	0.031
3.00	8.42	1.953	1.582	0.017	1.57	0.031
4.00	8.48	1.768	1.590	0.025	1.56	0.031
5.00	8.46	1.691	1.593	0.028	1.55	0.031
6.00	8.43	1.642	1.595	0.030	1.54	0.030
7.00	8.42	1.585	1.598	0.033	1.51	0.030
8.00	8.49	1.457	1.603	0.038	1.48	0.030

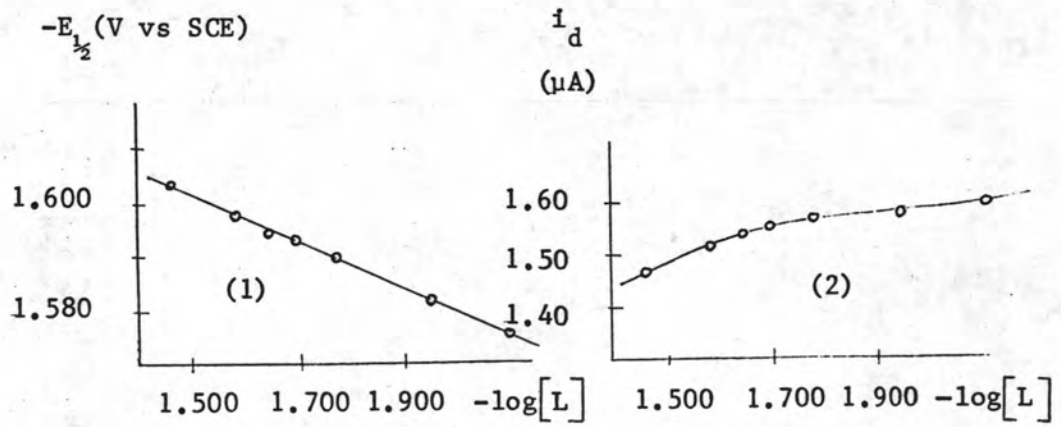

Figure 4.13 E Dependences of L-phenylalanate anion concentrations on $E_{1/2}$ (1) and i_d (2) of Mn(II) -L-phenylalanine system

Table 4.12 F Effects of L-threonine concentrations on the polarographic characteristics of Mn(II) -L-threonine system,

[HL] = L-threonine concentration and

[L] = L-threonate anion concentration

$[HL] \times 10^2$ (M)	pH	$-\log[L]$	$-E_{1/2}$ (V vs SCE)	$\Delta E_{1/2}$ (V)	i_d (μA)	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$ (V)
0.00	8.53	-	1.565	-	1.81	0.029
2.00	8.50	1.869	1.579	0.014	1.30	0.031
3.00	8.46	1.733	1.585	0.020	1.29	0.030
4.00	8.49	1.578	1.591	0.026	1.27	0.030
5.00	8.46	1.511	1.594	0.029	1.25	0.031
6.00	8.45	1.442	1.597	0.032	1.24	0.031
7.00	8.46	1.365	1.600	0.035	1.22	0.031
8.00	8.48	1.287	1.604	0.039	1.21	0.031

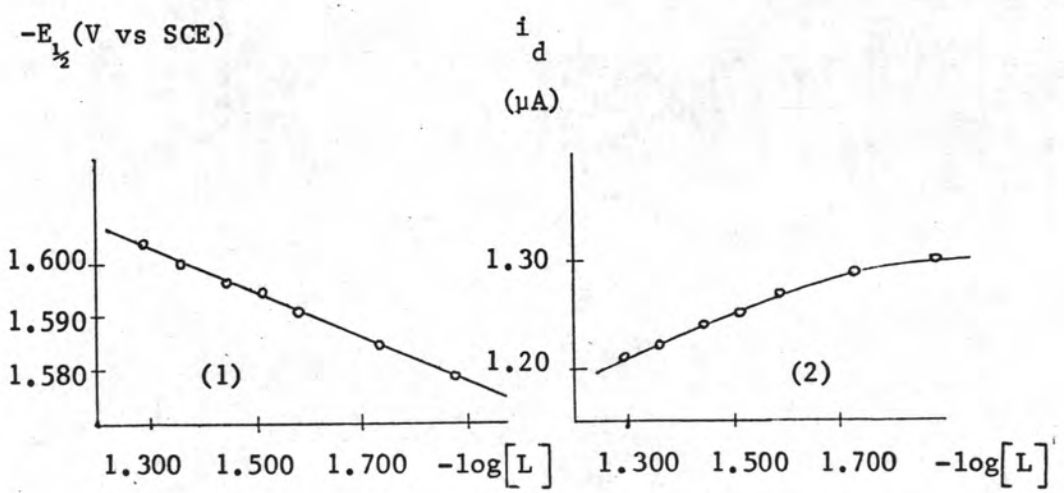

Figure 4.13 F Dependences of L-threonate anion concentrations on $E_{1/2}$ (1) and i_d (2) of Mn (II) -L-threonine system

Table 4.12 G Effects of L-tryptophan concentrations on the polarographic characteristics of Mn(II) -L-tryptophan system,

[HL] = L-tryptophan concentration and

[L] = L-tryptophanate anion concentration

$[HL]\times10^{2}$ (M)	pH	$-\log[L]$	$-E_{1/2}$ (V vs SCE)	$\Delta E_{1/2}$ (V)	i_d (μA)	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$ (V)
0.00	8.53	-	1.565	-	1.81	0.029
2.00	8.42	2.479	1.573	0.008	1.42	0.029
3.00	8.46	2.263	1.581	0.016	1.40	0.030
4.00	8.47	2.128	1.587	0.022	1.37	0.030
5.00	8.49	2.011	1.591	0.026	1.36	0.029
6.00	8.48	1.942	1.594	0.029	1.35	0.031
7.00	8.47	1.885	1.596	0.031	1.33	0.031
8.00	8.47	1.827	1.599	0.034	1.32	0.031

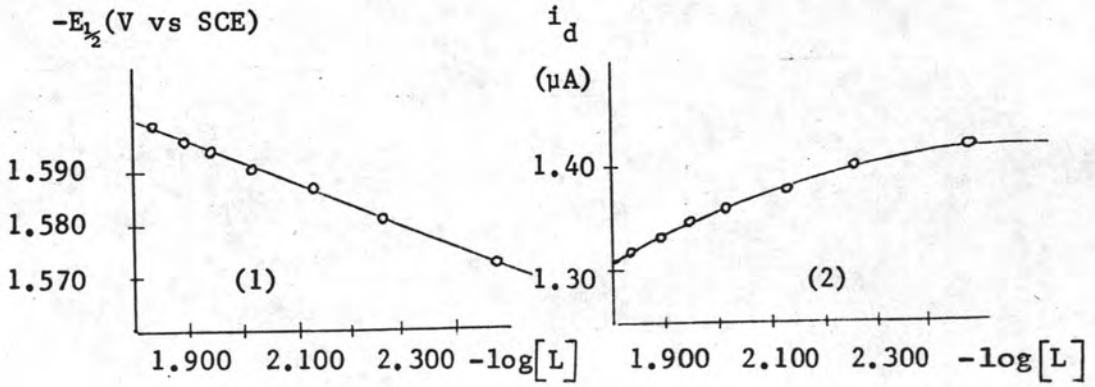

Figure 4.13 G Dependences of L-tryptophanate anion concentrations on $E_{1/2}$ (1) and i_d (2) of Mn(II) -L-tryptophan system

Table 4.12 H Effects of L-valine concentrations on the polarographic characteristics of Mn(II) -L-valine system,
[HL] = L-valine concentration and
[L] = L-valinate anion concentration

$[HL]\times10^{2}$ (M)	pH	$-\log[L]$	$-E_{1/2}$ (V vs SCE)	$\Delta E_{1/2}$ (V)	i_d (μA)	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$ (V)
0.00	8.53	-	1.565	-	1.81	0.029
2.00	8.45	2.389	1.568	0.003	1.39	0.031
3.00	8.47	2.193	1.576	0.011	1.37	0.030
4.00	8.51	2.028	1.583	0.018	1.35	0.030
5.00	8.54	1.901	1.588	0.023	1.34	0.031
6.00	8.52	1.842	1.590	0.025	1.32	0.031
7.00	8.51	1.785	1.592	0.027	1.32	0.031
8.00	8.50	1.737	1.594	0.029	1.31	0.031

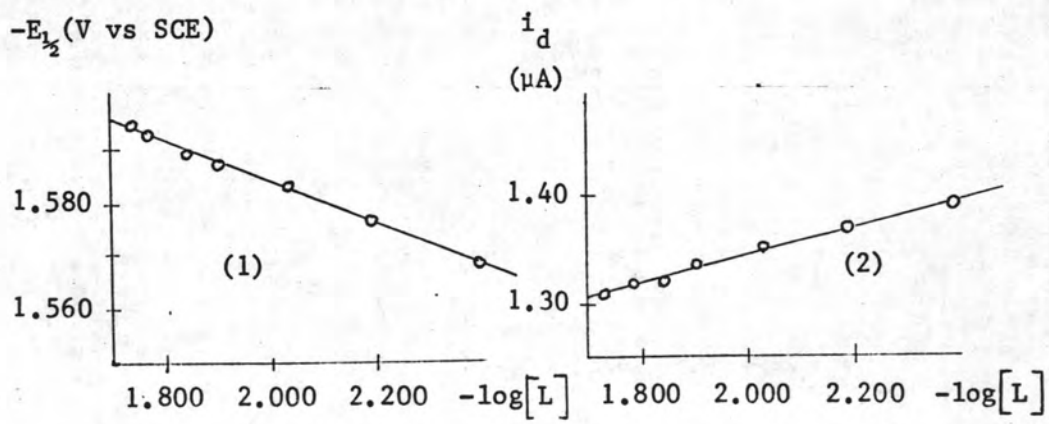

Figure 4.13 H Dependences of L-valinate anion concentrations on $E_{1/2}$ (1) and i_d (2) of Mn(II) -L-valine system

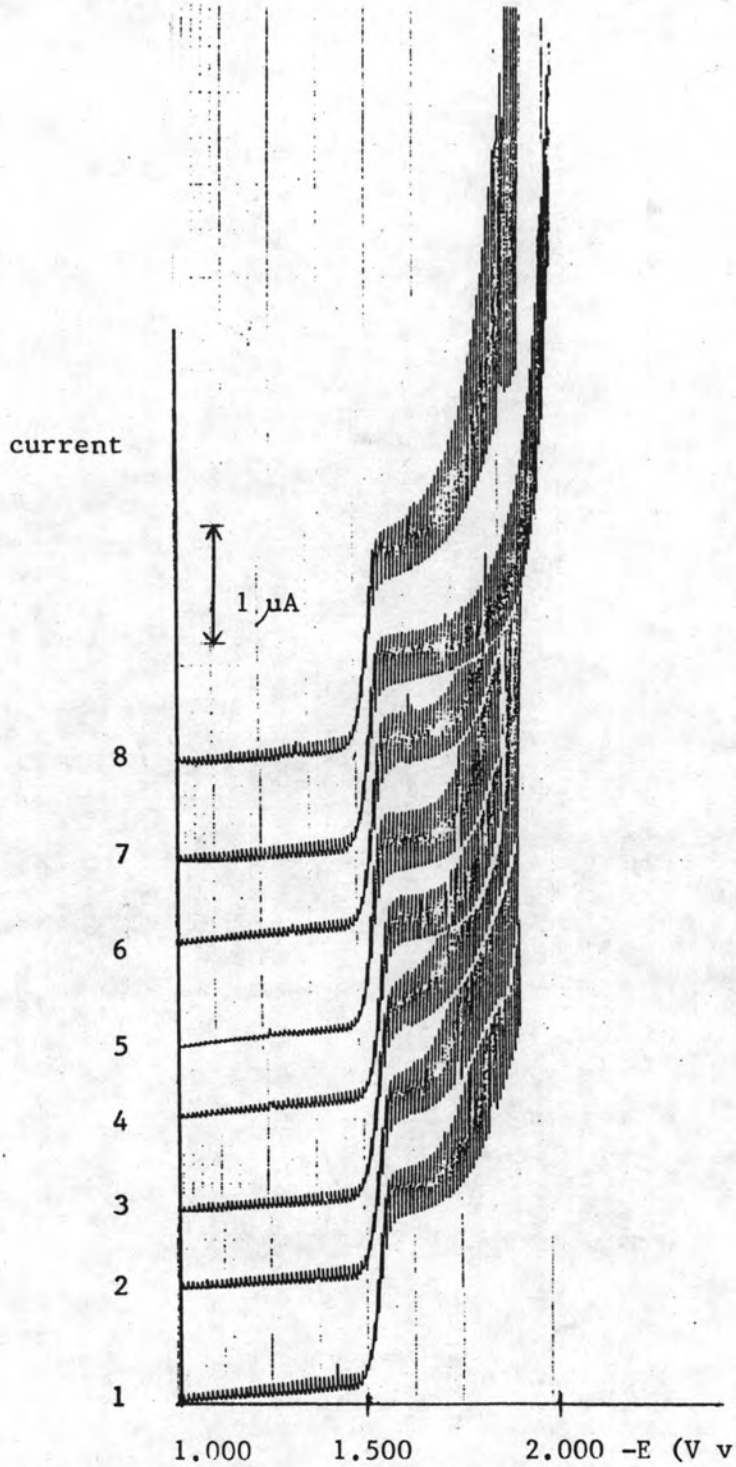

Figure 4.12 A Polarograms of 1.00×10^{-4} M Mn(II) ion and various concentrations of L-isoleucine in borate buffer and 0.10 M KCl; 1) 8.00×10^{-2} M pH 8.53, 2) 7.00×10^{-2} M pH 8.48, 3) 6.00×10^{-2} M pH 8.50, 4) 5.00×10^{-2} M pH 8.50, 5) 4.00×10^{-2} M pH 8.48, 6) 3.00×10^{-2} M pH 8.51, 7) 2.00×10^{-2} M pH 8.53 and 8) 0.00 M pH 8.53

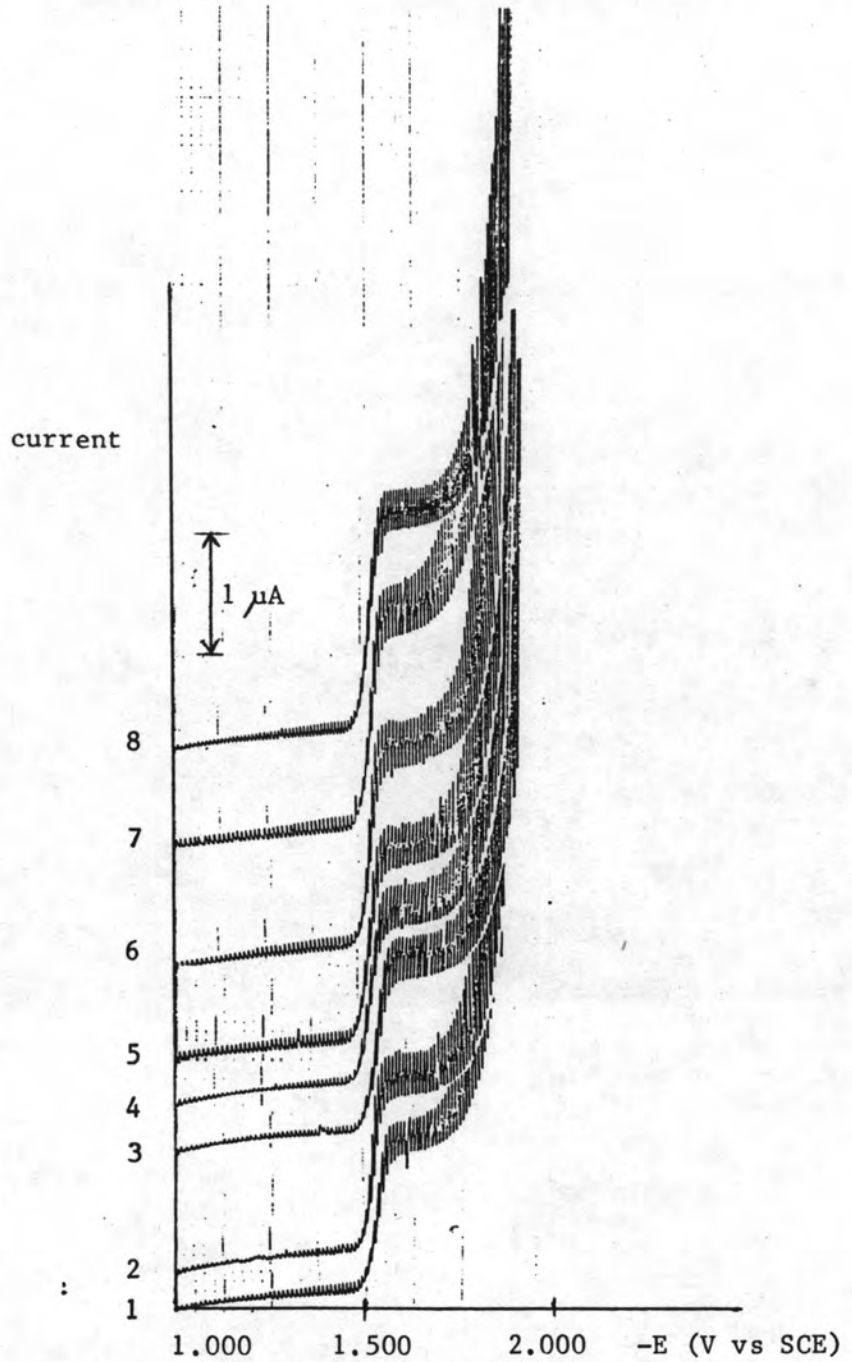

Figure 4.12 B Polarograms of 1.00×10^{-4} M Mn(II) ion and various concentrations of L-leucine in borate buffer and 0.10 M KCl ; 1) 8.00×10^{-2} M pH 8.52, 2) 7.00×10^{-2} M pH 8.51, 3) 6.00×10^{-2} M pH 8.51, 4) 5.00×10^{-2} M pH 8.51, 5) 4.00×10^{-2} M pH 8.52, 6) 3.00×10^{-2} M pH 8.54, 7) 2.00×10^{-2} M pH 8.54 and 8) 0.00 M pH 8.53

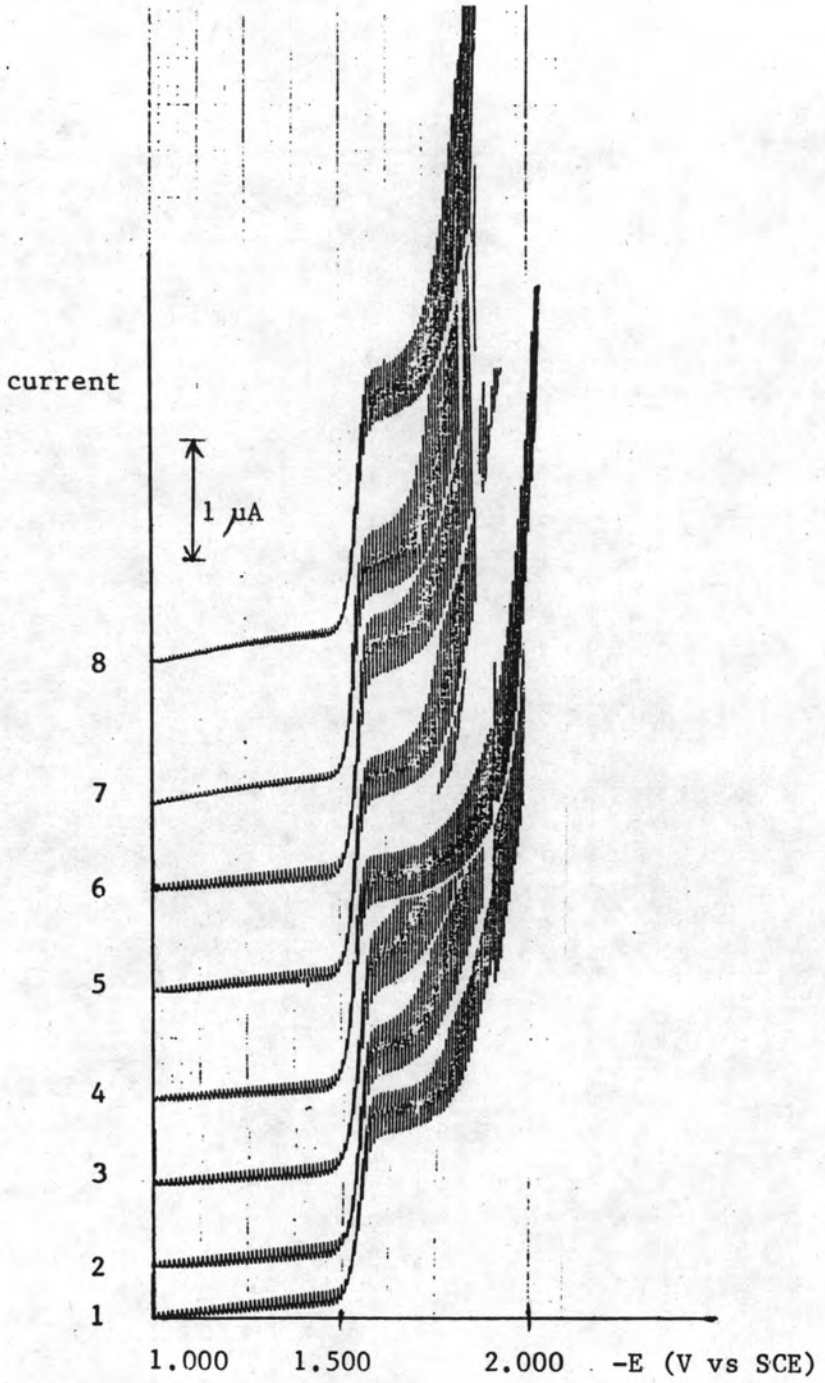

Figure 4.12 C Polarograms of 1.00×10^{-4} M Mn(II) ion and various concentrations of L-methionine in borate buffer and 0.10 M KCl. 1) 8.00×10^{-2} M pH 8.54, 2) 7.00×10^{-2} M pH 8.55, 3) 6.00×10^{-2} M pH 8.56, 4) 5.00×10^{-2} M pH 8.54, 6) 3.00×10^{-2} M pH 8.57, 7) 2.00×10^{-2} M pH 8.58 and 8) 0.00 M pH 8.53

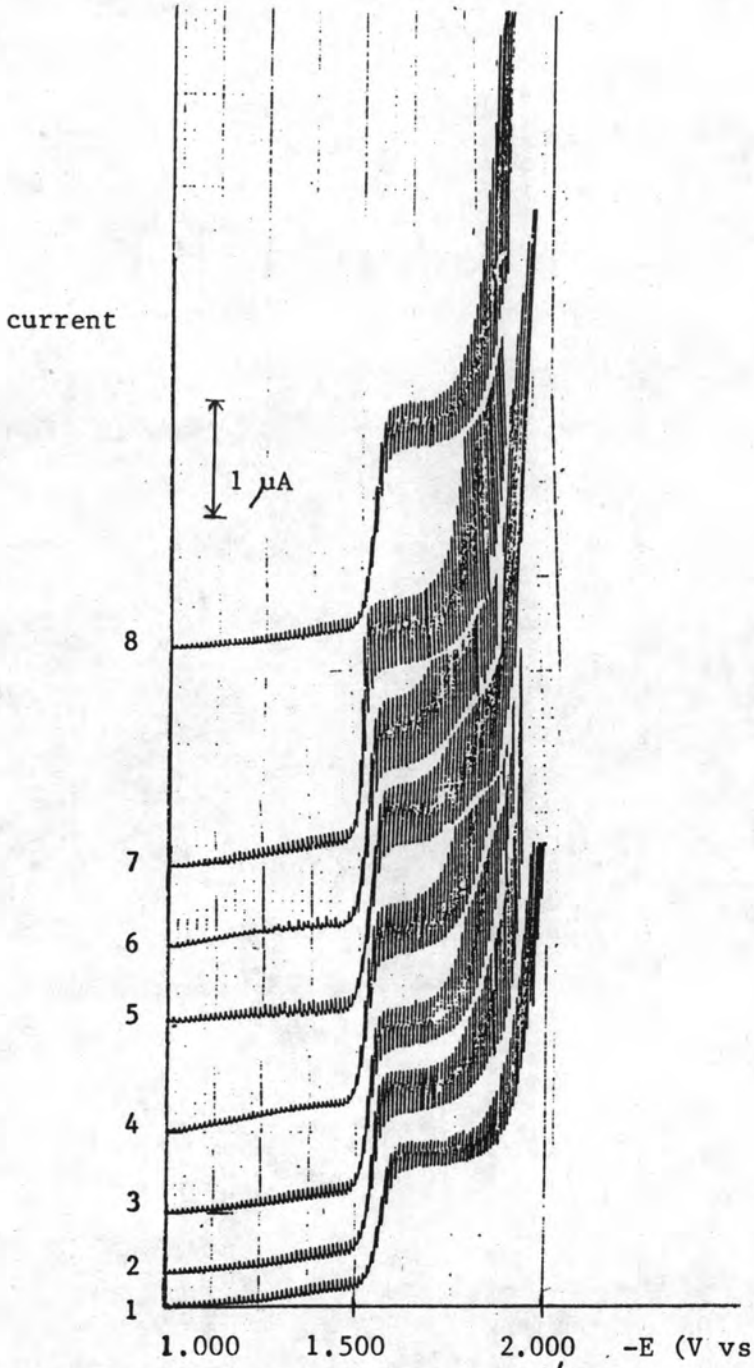

Figure 4.12 D Polarograms of 1.00×10^{-4} M Mn(II) ion and various concentrations of L-phenylalanine in borate buffer and 0.10 M KCl ; 1) 8.00×10^{-2} M pH 8.49, 2) 7.00×10^{-2} M pH 8.42, 3) 6.00×10^{-2} M pH 8.43, 4) 5.00×10^{-2} M pH 8.46, 5) 4.00×10^{-2} M pH 8.48, 6) 3.00×10^{-2} M pH 8.42, 7) 2.00×10^{-2} M pH 8.45 and 8) 0.00 M pH 8.53

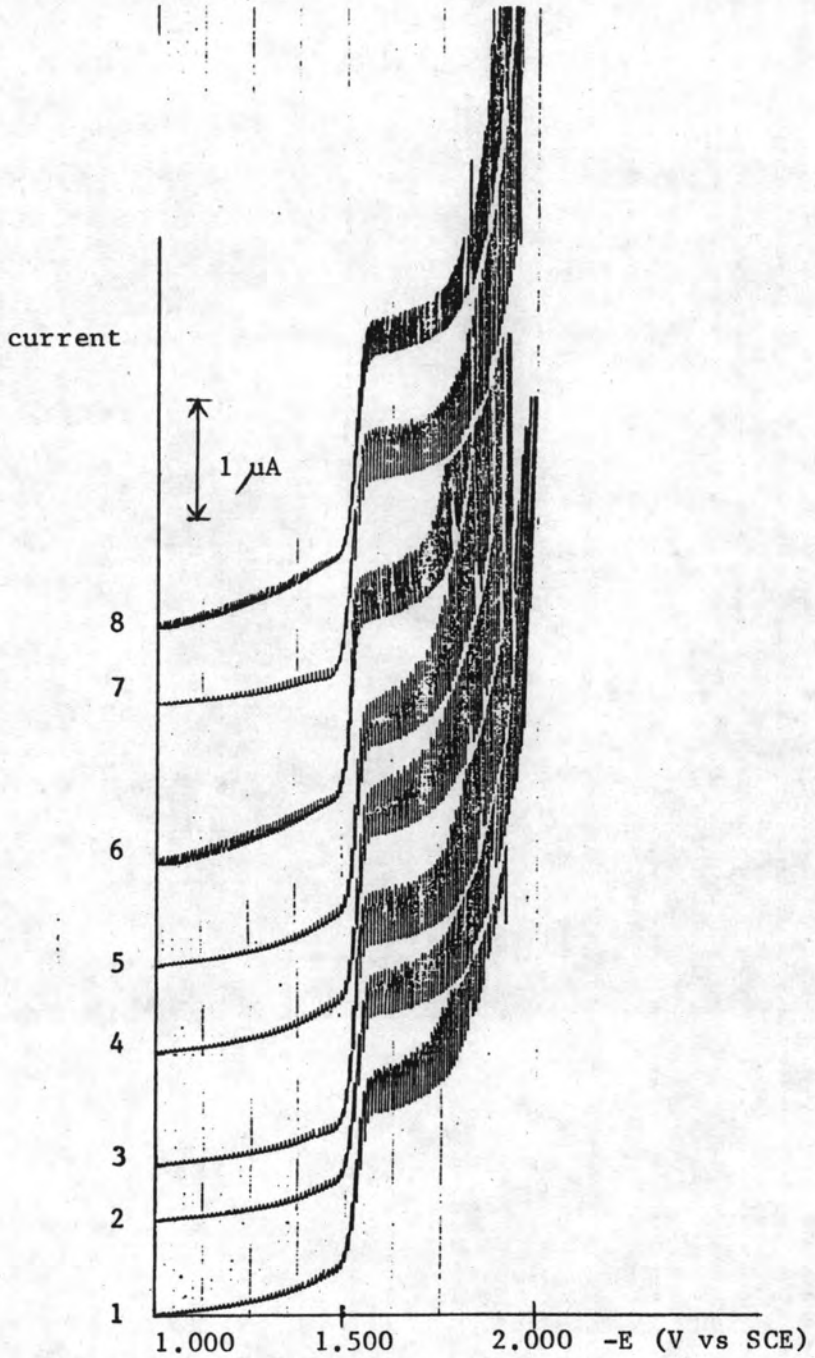

Figure 4.12 E Polarograms of 1.00×10^{-4} M Mn(II) ion and various concentrations of L-tryptophan in borate buffer and 0.10 M KCl ; 1) 8.00×10^{-2} M pH 8.47, 2) 7.00×10^{-2} M pH 8.47, 3) 6.00×10^{-2} M pH 8.48 , 4) 5.00×10^{-2} M pH 8.49, 5) 4.00×10^{-2} M pH 8.47, 6) 3.00×10^{-2} M pH 8.46, 7) 2.00×10^{-2} M pH 8.42 and 8) 0.00 M pH 8.53

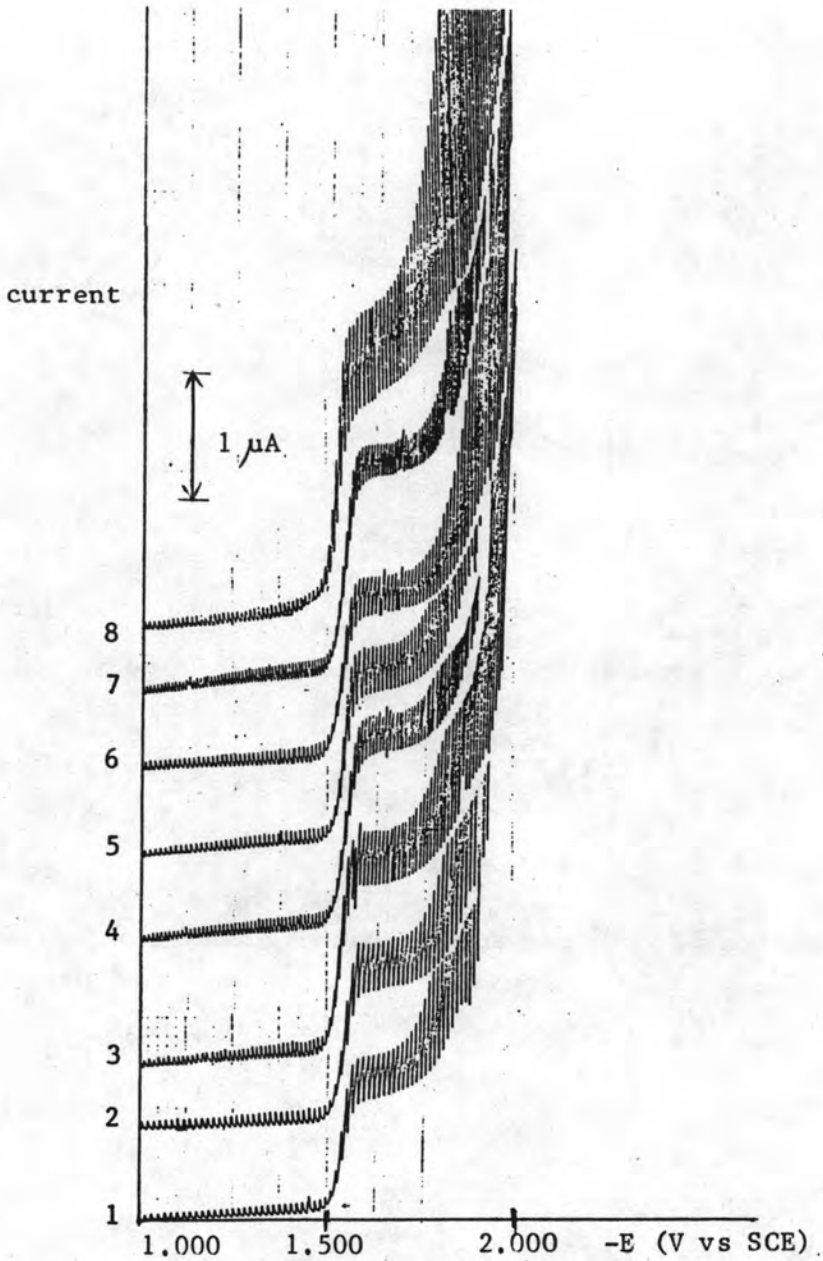

Figure 4.12 F Polarograms of 1.00×10^{-4} M Mn(II) ion and vacious concentrations of L-valine in borate buffer and 0.10 M KCl; 1) 8.00×10^{-2} M pH 8.50, 2) 7.00×10^{-2} M pH 8.51, 3) 6.00×10^{-2} M pH 8.52, 4) 5.00×10^{-2} M pH 8.54, 5) 4.00×10^{-2} M pH 8.51, 6) 3.00×10^{-2} M pH 8.47, 7) 2.00×10^{-2} M pH 8.45 and 8) 0.00 M pH 8.53

the essential amino acid anion increased, the $E_{\frac{1}{2}}$ of Mn(II)-essential amino acid systems shifted to more negative potential and the i_d decreased (see Table 4.12 A - 4.12 H and Figure 4.13 A - 4.13 H). These evidences showed that the complex formations were taken place in the solutions of each system. The values evaluated from $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ (see Table 4.12 A - 4.12 H) showed that the reductions of Mn(II) ion in the presence of these essential amino acids were reversible. The effect of h in the range of 40.0 - 70.0 cm at pH 8.5 on i_d for each system was shown respectively in Table 4.13 A - 4.13 H and the plots of i_d vs $h^{\frac{1}{2}}$ giving linear lines passed through the origin for all systems (see Figure 4.14 A - 4.14 H) showed that these systems were diffusion-controlled. The plots of $E_{\frac{1}{2}}$ vs log [L] gave the one linearity for all systems (see Figure 4.13 A - 4.13 H) thereby the single complex was formed. In order to confirm these results, the plots of $\Delta E_{\frac{1}{2}}$ vs log [L] by least squares treatment were performed and they also showed one linear portion for each system (see Figure 4.15 A - 4.15 H). The value of j corresponding to the value of log β_j of the complexes was worked out from the slope and the intercept of the plots of $\Delta E_{\frac{1}{2}}$ vs log [L], respectively, by equation (2.22) and as in the preceding section. The values of the linear correlation coefficient (γ), the slope and the intercept of each linear portion from the plots of $\Delta E_{\frac{1}{2}}$ vs log [L] of Mn(II)-essential amino acid complexes (Figure 4.15 A - 4.15 H) including the corresponding values of j and log β_j were colloected as shown in Table 4.14. From Table 4.14, the values of j became 1 ($j \simeq 1$), therefore it could be said that the composition of the Mn(II) ion to L-isoleucine, Mn(II) ion to L-leucine, Mn(II) ion to L-methionine, Mn(II) ion to L-phenylalanine, Mn(II) ion to L-threonine,

Table 4.13 A Effect of h on i_d of Mn(II) -L-isoleucine system

h(cm)	$h^{1/2}(cm^{1/2})$	$i_d(\mu A)$
40.0	6.32	1.48
50.0	7.07	1.67
60.0	7.75	1.85
70.0	8.37	2.01

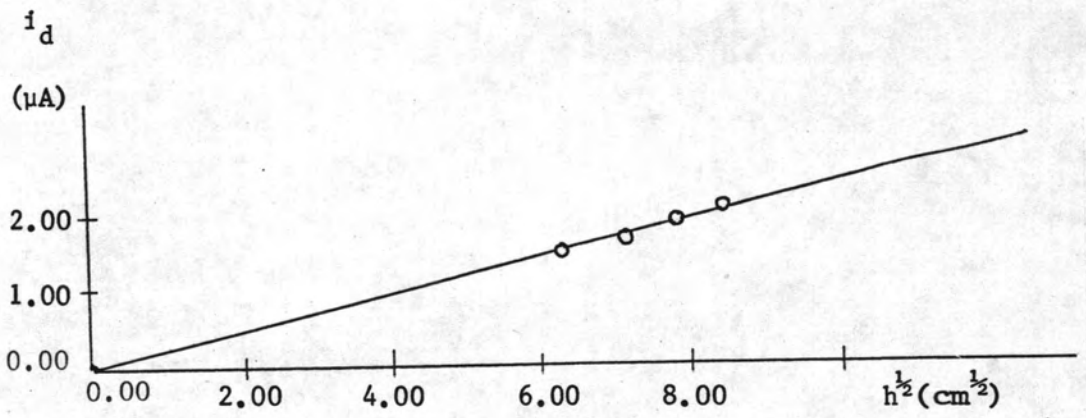

Figure 4.14 A Dependence of $h^{1/2}$ on i_d of Mn(II) -L-isoleucine system

Table 4.13 B Effect of h on i_d of Mn(II) -L-leucine system

h(cm)	$h^{\frac{1}{2}}(cm^{\frac{1}{2}})$	$i_d(\mu A)$
40.0	6.32	1.58
50.0	7.07	1.77
60.0	7.75	1.96
70.0	8.37	2.23

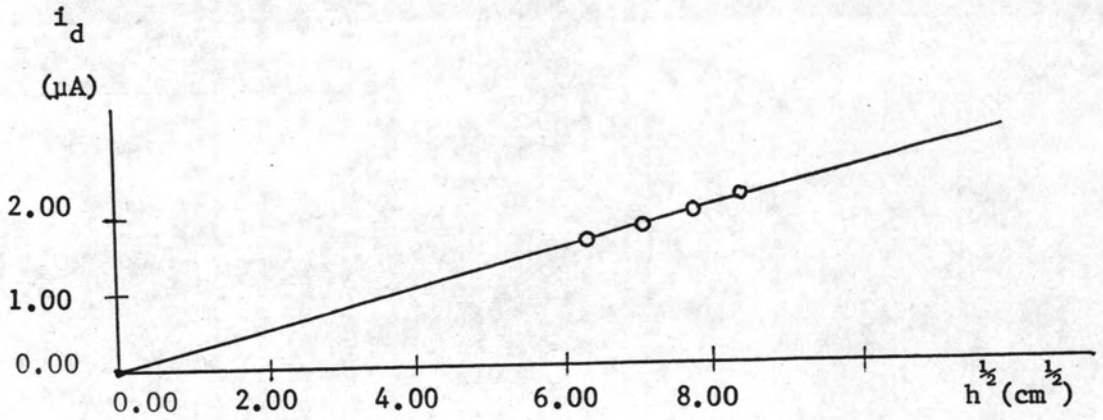

Figure 4.14 B Dependence of $h^{\frac{1}{2}}$ on i_d of Mn(II) -L-leucine system

Table 4.13 D Effect of h on i_d of Mn(II) -L-methionine system

h(cm)	$h^{\frac{1}{2}}(cm^{\frac{1}{2}})$	$i_d(\mu A)$
40.0	6.32	1.69
50.0	7.07	1.92
60.0	7.75	2.15
70.0	8.37	2.42

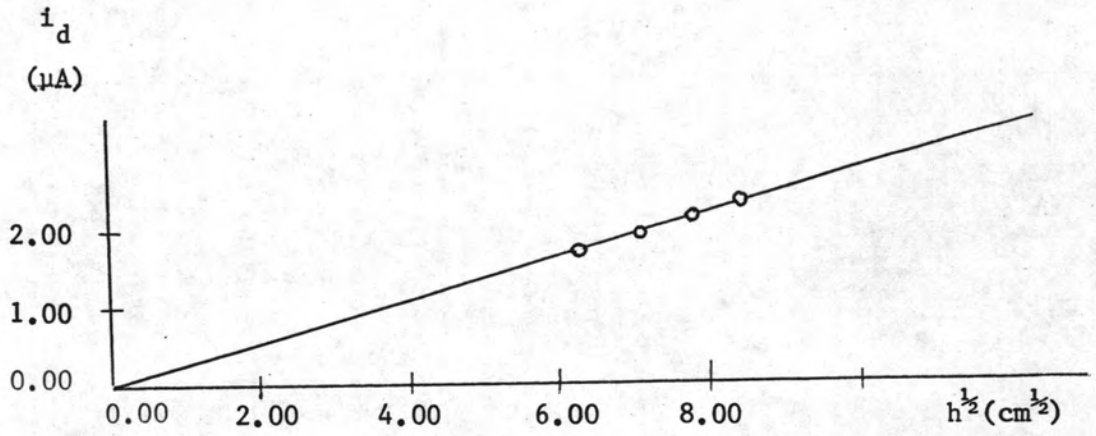

Figure 4.14 D Dependence of $h^{\frac{1}{2}}$ on i_d of Mn(II) -L-methionine system

Table 4.13 E Effect of h on i_d of Mn(II) -L-phenylalanine system

h(cm)	$h^{1/2}(cm^{1/2})$	$i_d(\mu A)$
40.0	6.32	1.48
50.0	7.07	1.62
60.0	7.75	1.88
70.0	8.37	2.08

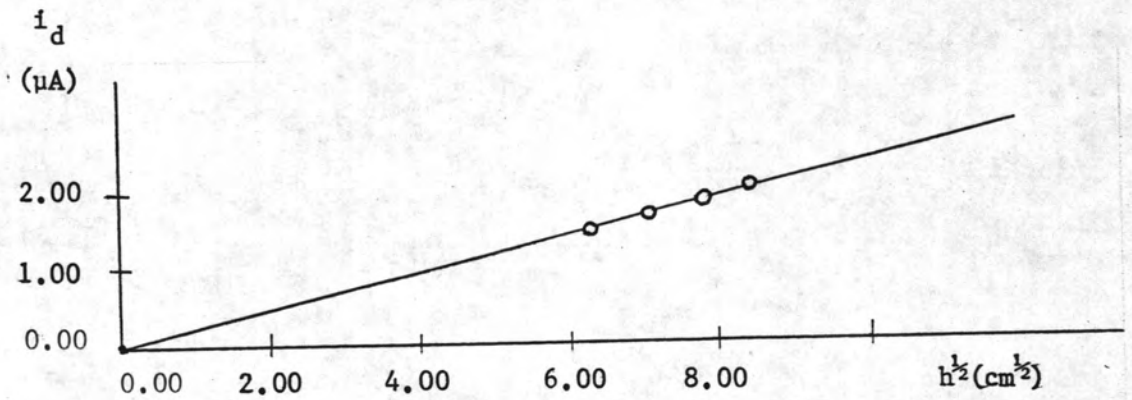

Figure 4.14.E Dependence of $h^{1/2}$ on i_d of Mn(II) -L-phenylalanine system

Table 4.13 F Effect of h on i_d of Mn(II) -L-threonine system

h(cm)	$h^{1/2}(cm^{1/2})$	$i_d(\mu A)$
40.0	6.32	1.21
50.0	7.07	1.36
60.0	7.75	1.52
70.0	8.37	1.71

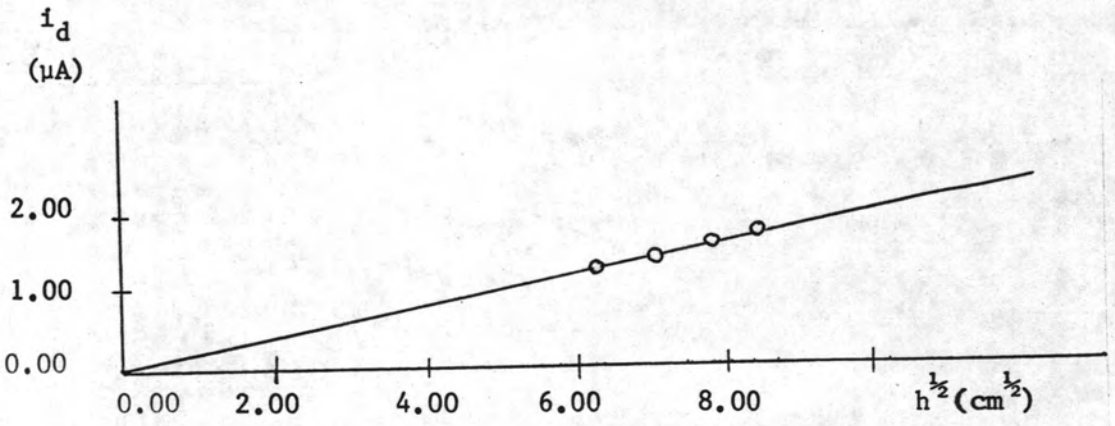

Figure 4.14 F Dependence of $h^{1/2}$ on i_d of Mn (II) -L-threonine system

Table 4.13 G Effect of h on i_d of Mn(II) -L-tryptophan system

h(cm)	$h^{1/2}(cm^{1/2})$	$i_d(\mu A)$
40.0	6.32	1.42
50.0	7.07	1.54
60.0	7.75	1.77
70.0	8.37	1.92

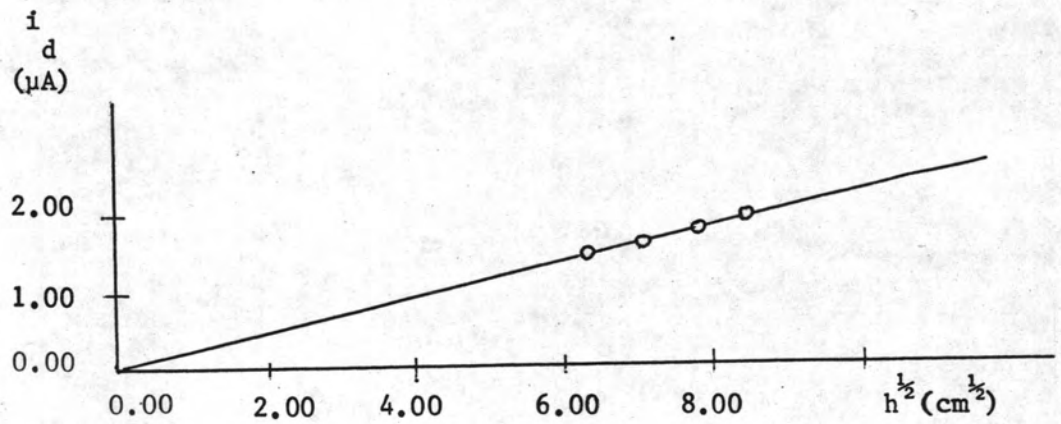

Figure 4.14 G Dependence of h on i of Mn(II) -L-tryptophan system

Table 4.13 H Effect of h on i_d of Mn(II) -L-valine system

h(cm)	$h^{\frac{1}{2}}(cm^{\frac{1}{2}})$	$i_d(\mu A)$
40.0	6.32	1.31
50.0	7.07	1.46
60.0	7.75	1.62
70.0	8.37	1.81

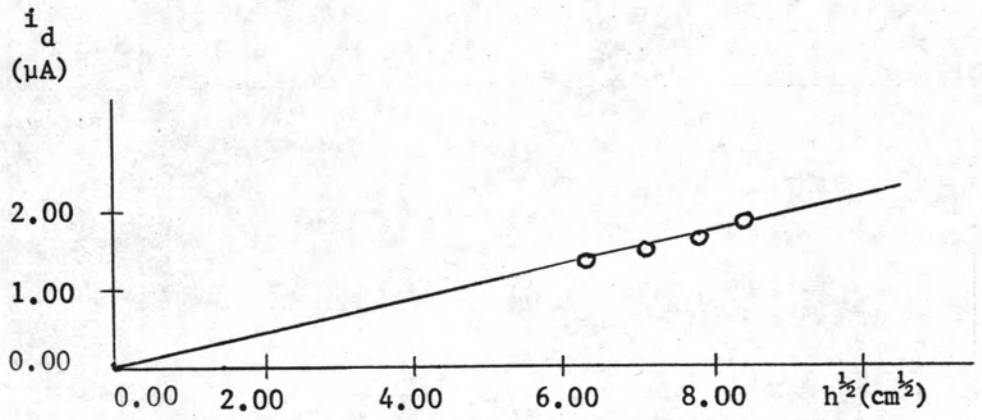

Figure 4.14 H Dependence of $h^{\frac{1}{2}}$ on i_d of Mn(II) -L-valine system

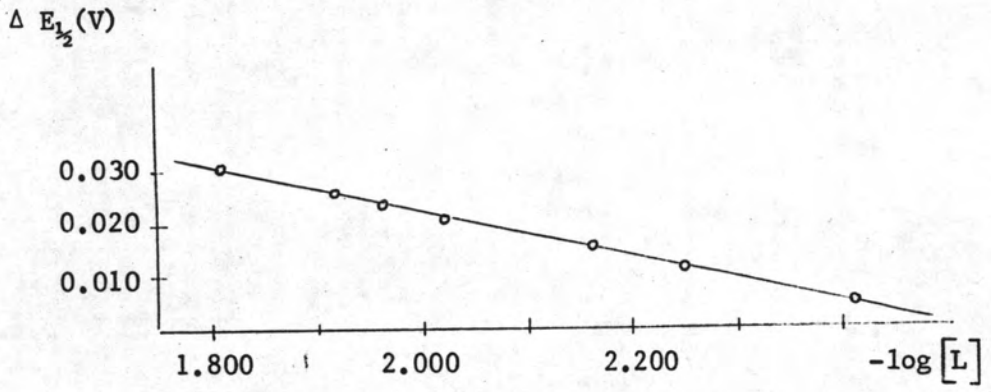

Figure 4.15 A Dependence of L-isoleucinate anion concentrations on $\Delta E_{\frac{1}{2}}$ of Mn(II) -L-isoleucine system

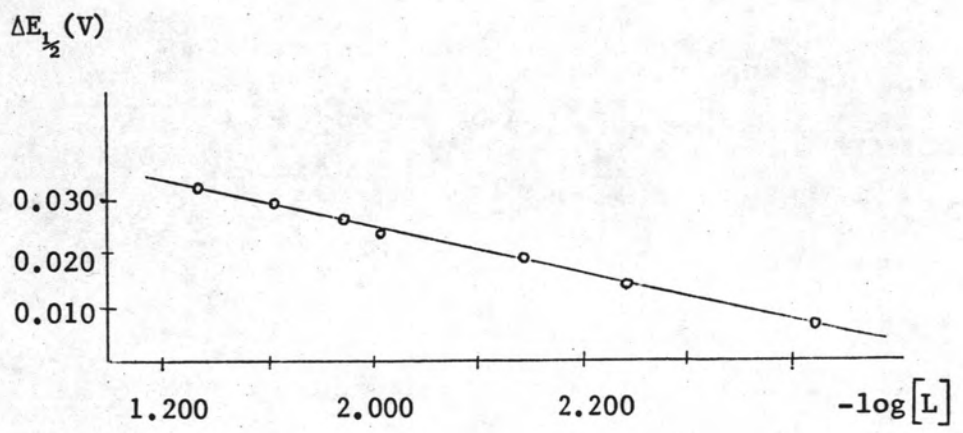

Figure 4.15 B Dependence of L-leucinate anion concentrations on $\Delta E_{\frac{1}{2}}$ of Mn(II) -L-leucine system

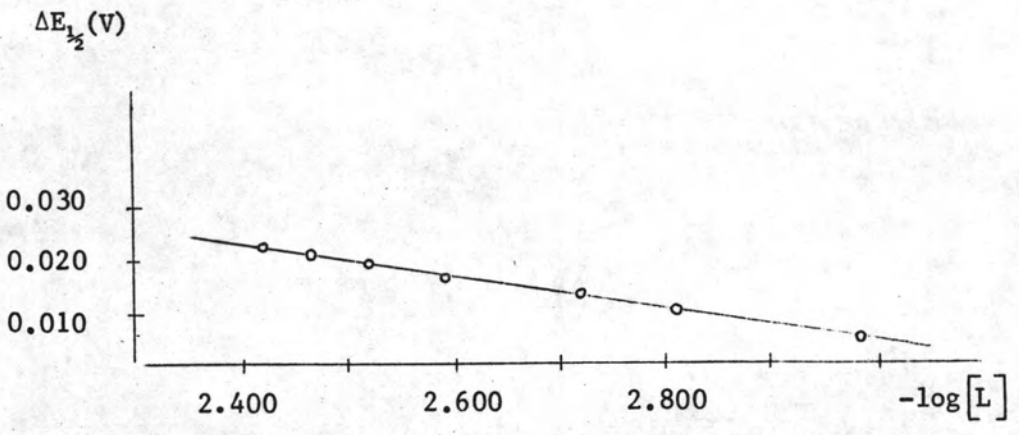

Figure 4.15 D Dependence of L-methionate anion concentrations on $\Delta E_{1/2}$ of Mn(II) -L-methionine system

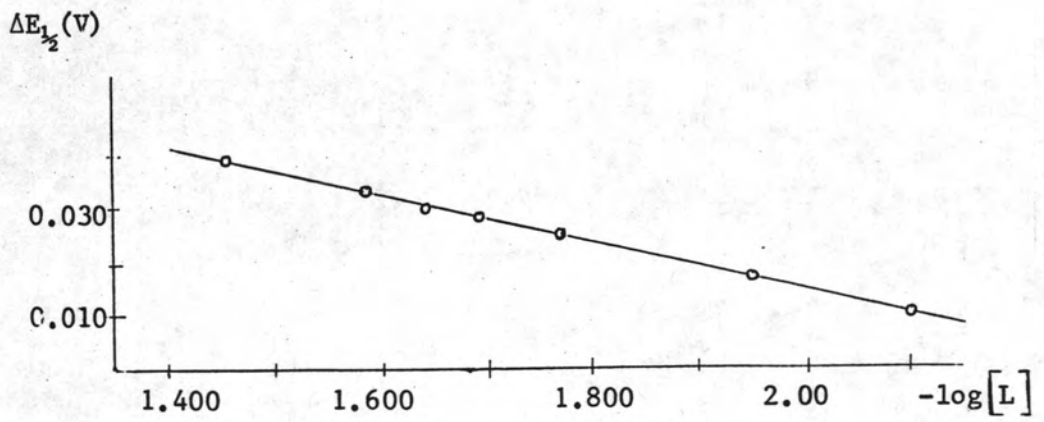

Figure 4.15 E Dependence of L-phenylalanate anion concentrations on $\Delta E_{1/2}$ of Mn(II) -L-phenylalanine system

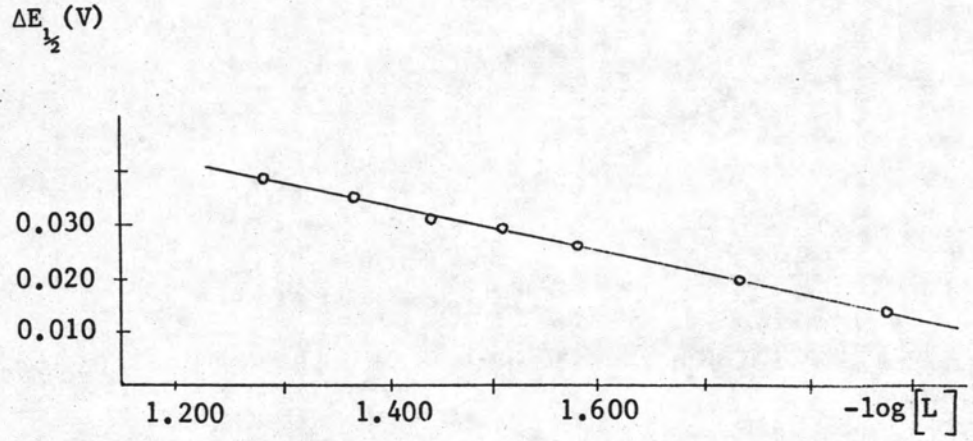

Figure 4.15 F Dependence of L-threonate anion concentrations on $\Delta E_{1/2}$ of Mn(II) -L-threonine system

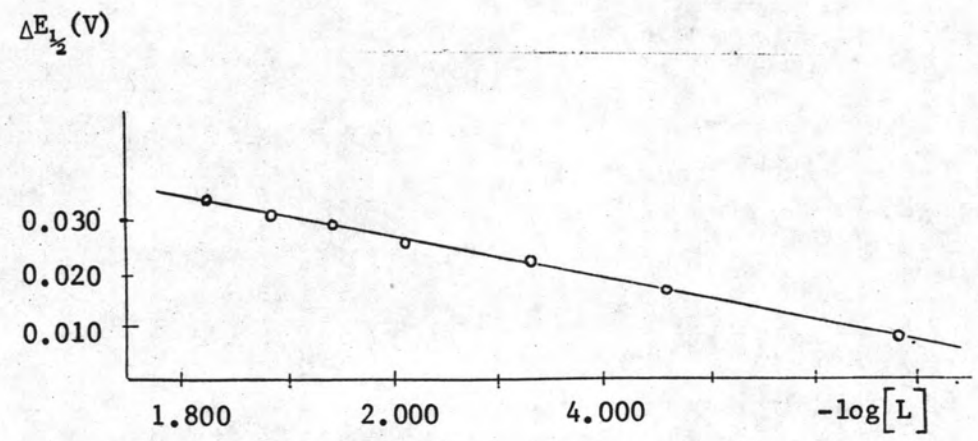

Figure 4.15 G Dependence of L-tryptophanate anion concentrations on$\Delta E_{1/2}$ of Mn(II) -L-tryptophan system

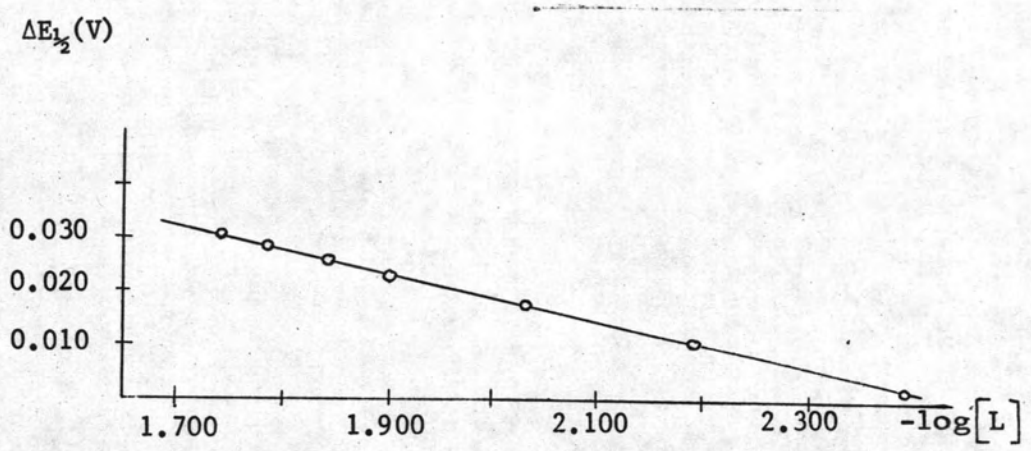

Figure 4.15 H Dependence of L-valinate anion concentrations on $\Delta E_{1/2}$ of Mn(II) -L-valine system

Table 4.14 Obtained values from the linear plot of $\Delta E_{\frac{1}{2}}$ vs log [L] from Mn(II)-essential amino acid complexes by polarographic technique

anion of Mn complex	linear correlation coefficient(γ)	slope	j	inter-cept	log β_j	Remarks
L-isoleucine	0.999	0.041	1.33	0.104	3.38	
L-leucine	0.999	0.043	1.40	0.111	3.61	
L-lysine	-	-	-	-	-	ill-defined wave
L-methionine	0.999	0.032	1.04	0.099	3.22	
L-phenylalanine	0.999	0.042	1.36	0.100	3.25	
L-threonine	0.999	0.042	1.36	0.093	3.02	
L-tryptophan	0.999	0.039	1.27	0.106	3.45	
L-valine	0.998	0.040	1.30	0.098	3.19	

Mn(II) ion to L-tryptophan and Mn(II) ion to L-valine was 1:1 in each case.

4.4.2.3 Pb(II)-Essential Amino Acids Systems

The solutions containing 1.00×10^{-4} M Pb(II) ion in the presence of 2.00×10^{-2} M essential amino acid were studied by varying pH of the solution. The effects of pH on the polarographic characteristics of each system are shown respectively in Table 4.15 A - 4.15 H and the dependences of pH on the polarographic characteristics were plotted as shown respectively for each system in Figure 4.16 A - 4.16 H. In case of Pb(II)-L-lysine system, no shifting in $E_{1/2}$ as pH increased and the precipitate occurred at pH above 6.0 (see Table 4.15 C and Figure 4.16 C). Therefore, pH 5.5 was chosen to study the complex formation of the Pb(II)-L-lysine system. In case of those systems other than the Pb(II)-L-lysine system, the negative shift in $E_{1/2}$ increased as pH increased and the precipitation occurred at pH above 7.0 for the systems of Pb(II)-L-isoleucine, Pb(II)-L-leucine, Pb(II)-L-methionine, Pb(II)-L-tryptophan and Pb(II)-L-valine, at pH above 6.0 for the Pb(II)-L-threonine system and at pH above 7.9 for the Pb(II)-L-phenylalanine system (see Table 4.15 A - 4.15 H and Figure 4.16 A - 4.16 H). To prevent the precipitation, therefore, the pH 6.5 was chosen to study the complex formation for the systems of Pb(II)-L-isoleucine, Pb(II)-L-leucine, Pb(II)-L-methionine, Pb(II)-L-tryptophan and Pb(II)-L-valine, the pH 5.5 for the Pb(II)-L-threonine system and the pH 7.4 for the Pb(II)-L-phenylalanine system. At constant pH of each system mentioned above, the solutions containing 1.00×10^{-4} M Pb(II) ion in the presence of essential amino acid were

Table 4.15 A Effects of pH on the polarographic characteristics of Pb(II)-L-isoleucine system

pH	$-E_{\frac{1}{2}}$ (V vs SCE)	i_d (μA)	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$ (V)
4.00	0.495	1.62	0.029
4.95	0.495	1.61	0.029
5.87	0.496	1.58	0.030
6.47	0.497	1.57	0.030

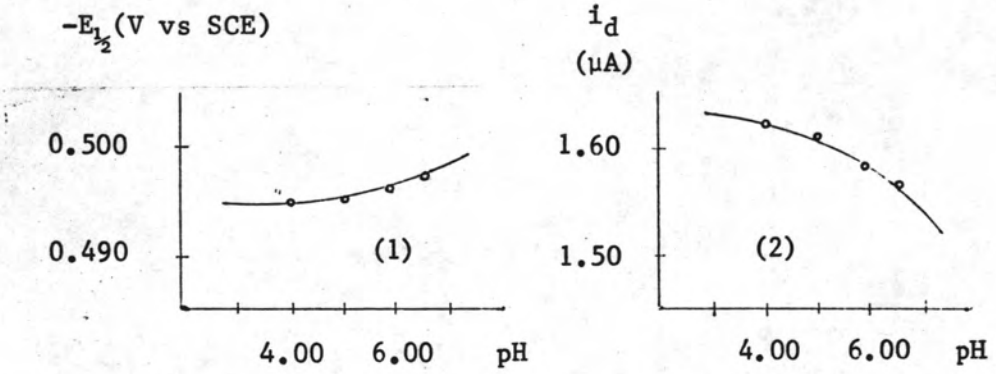

Figure 4.16 A Dependences of pH on $E_{\frac{1}{2}}$ (1) and i_d (2) of Pb(II) -L-isoleucine system

Table 4.15 B Effects of pH on the polarographic characteristics of Pb(II)-L-leucine system

pH	$-E_{\frac{1}{2}}$ (V vs SCE)	i_d (μA)	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$ (V)
2.97	0.495	1.61	0.029
4.05	0.498	1.59	0.030
5.04	0.500	1.56	0.030
5.47	0.500	1.55	0.029
6.03	0.502	1.52	0.031
6.52	0.504	1.49	0.029

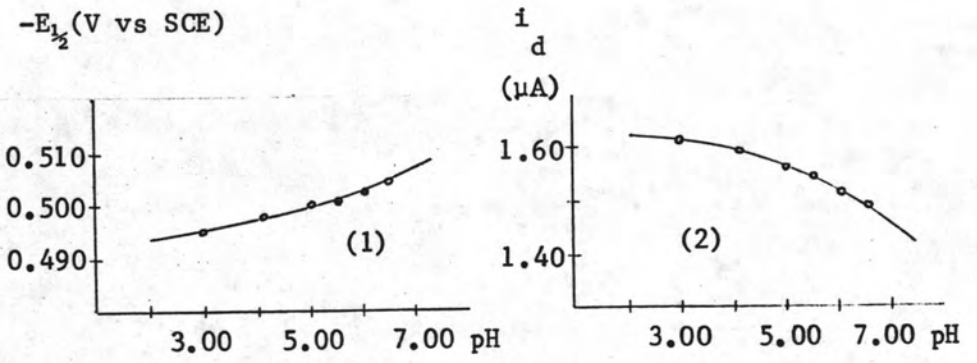

Figure 4.16 B Dependences of pH on $E_{\frac{1}{2}}$ (1) and i_d (2) of Pb(II) -L-leucine system

Table 4.15 C Effects of pH on the polarographic characteristics of Pb(II) -L-lysine system

pH	$-E_{\frac{1}{2}}$ (V vs SCE)	i_d (μA)	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$ (V)
3.00	0.495	1.70	0.030
4.03	0.495	1.71	0.030
5.18	0.495	1.71	0.030

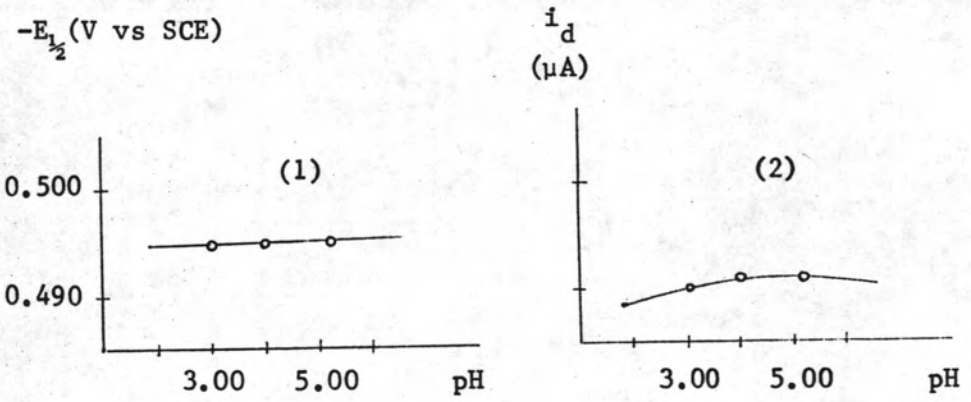

Figure 4.16 C Dependences of pH on $E_{\frac{1}{2}}$ (1) and i_d (2) of Pb(II) -L-lysine system

Table 4.15 D Effects of pH on the polarographic characteristics of Pb(II) -L-methionine system

pH	$-E_{\frac{1}{2}}$ (V vs SCE)	i_d (μA)	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$ (V)
4.03	0.507	1.51	0.029
5.55	0.510	1.49	0.029
6.55	0.513	1.47	0.030

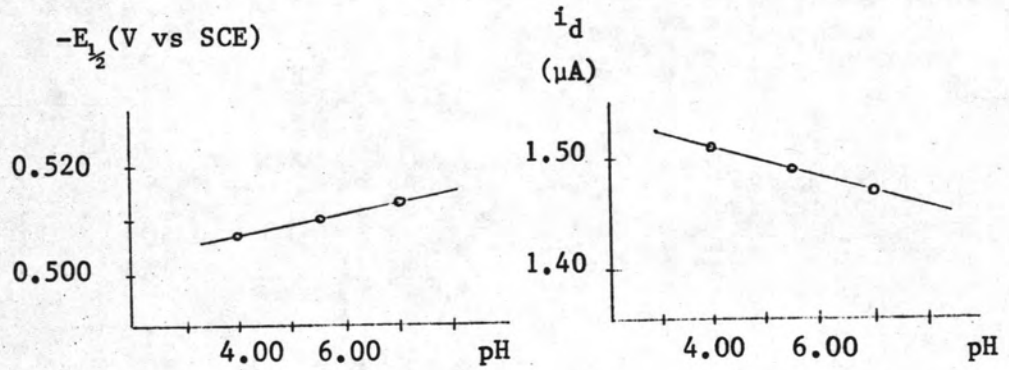

Figure 4.16 D Dependences of pH on $E_{\frac{1}{2}}$ (1) and i_d(2) of Pb (II) -L-methionine system

Table 4.15 E Effects of pH on the polarographic characteristics of Pb(II) -L-phenylalanine system

pH	$-E_{1/2}$ (V vs SCE)	i_d (μA)	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$ (V)
2.76	0.529	1.52	0.029
3.97	0.530	1.50	0.030
4.91	0.530	1.47	0.029
5.67	0.533	1.45	0.030
6.04	0.535	1.44	0.051
7.01	0.540	1.44	0.031
7.44	0.543	1.43	0.031

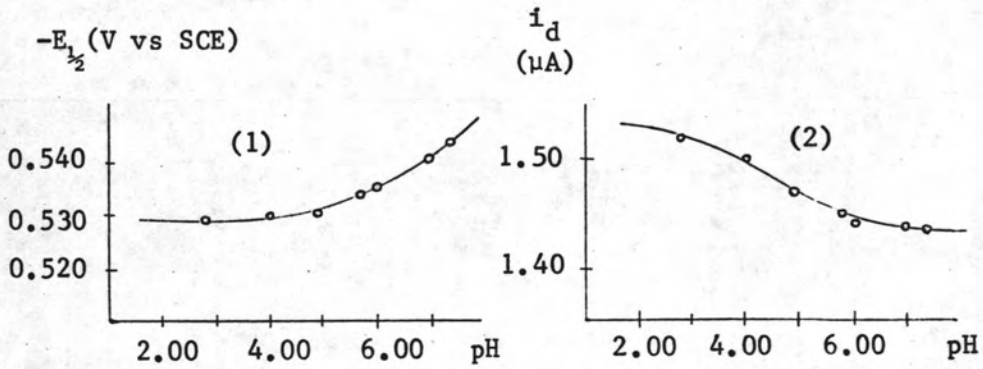

Figure 4.16 E Dependences of pH on $E_{1/2}$ (1) and i_d (2) of Pb (II) -L-phenylalanine system

Table 4.15 F Effects of pH on the polarographic characteristic of Pb (II)-L-threonine system

pH	$-E_{1/2}$ (V vs SCE)	i_d (μA)	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$ (V)
3.01	0.497	1.45	0.029
4.03	0.499	1.44	0.029
5.07	0.500	1.43	0.030
5.45	0.503	1.42	0.030

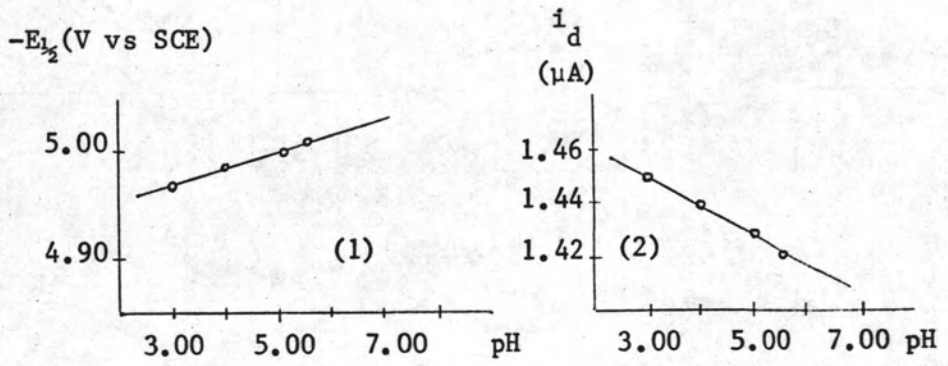

Figure 4.16 F Dependences of pH on $E_{1/2}$ (1) and i_d (2) of Pb (II) -L-threonine system

Table 4.15 G Effects of pH on the polarographic characteristics of Pb (II) -L- tryptophan system

pH	$-E_{1/2}$ (V vs SCE)	i_d (A)	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$ (V)
4.03	0.515	1.32	0.030
4.97	0.517	1.25	0.031
6.15	0.518	1.19	0.030
6.75	0.520	1.15	0.030

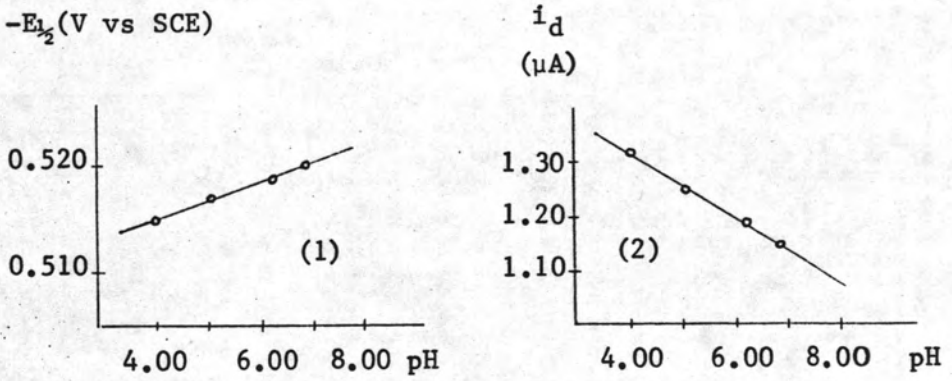

Figure 4.16 G Dependences of pH on $E_{1/2}$ (1) and i_d (2) of Pb(II) -L-tryptophan system

Table 4.15 H Effects of pH on the polarographic characteristics of Pb (II)-L-valine system

pH	$-E_{1/2}$ (V vs SCE)	i_d (μA)	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$ (V)
2.05	0.497	2.08	0.029
3.07	0.499	2.05	0.029
4.03	0.500	2.03	0.029
4.98	0.503	2.00	0.029
5.97	0.505	1.92	0.030

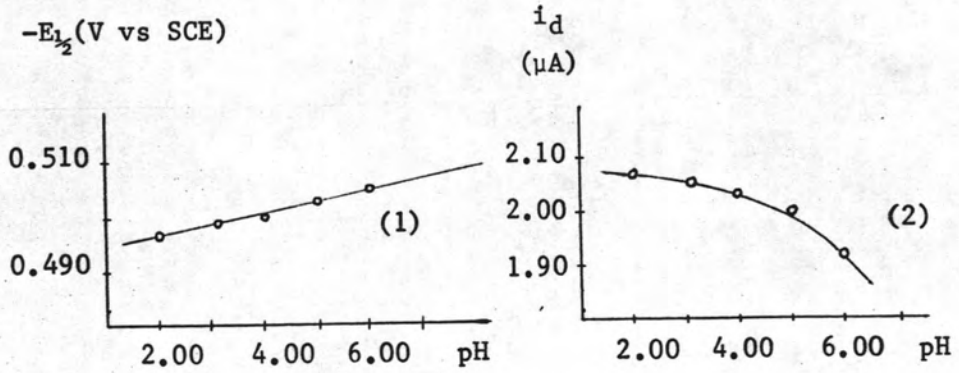

Figure 4.16 H Dependences of pH on $E_{1/2}$ (1) and i_d (2) of Pb(II) -L-valine system

studied by varying the essential amino acid concentrations in the range of 2.00×10^{-2} - 8.00×10^{-2} M. The effects of the essential amino acid concentrations on the polarographic characteristics of each system are shown respectively in Table 4.16 A - 4.16 H. The polarograms of the systems of Pb(II)-L-isoleucine and Pb(II)-L-threonine at various excess concentrations of the essential amino acids (in the range of 2.00×10^{-2} - 8.00×10^{-2} M) are also shown respectively in Figure 4.17 A and 4.17 B. The dependences of the essential amino acid anion concentrations on the polarographic characteristics were plotted as shown respectively for each system in Figure 4.18 A - 4.18 H. At constant pH of each system mentioned above, while the concentration of the essential amino acid anion increased, the $E_{\frac{1}{2}}$ of Pb(II)-essential amino acid systems shifted to more negative potential and the i_d decreased (see Table 4.16 A - 4.16 H and Figure 4.18 A - 4.18 H). Exceptionally, the $E_{\frac{1}{2}}$ of Pb(II)-L-lysine systems did not shifted to more negative potentials although the i_d decreased as the concentrations of L-lysinate anion increased at the pH 5.5 (see Table 4.16 C and Figure 4.18 C). These evidences showed that the complex formations were taken place in the solution of each system, excepted of Pb(II)-L-lysine system. The values evaluated from $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ (see Table 4.16 A - 4.16 H) showed that the reductions of Pb (II) ion in presence of these essential amino acids were reversible. The effect of h in the range of 40.0 - 70.0 cm (at constant pH of each system mentioned above) on i_d for each system was shown respectively in Table 4.17 A - 4.17 H and the plots of i_d vs $h^{\frac{1}{2}}$ giving linear lines passed through the origin for all systems (see Figure 4.19 A - 4.19 H) showed that these systems were diffusion-controlled. The plots of $E_{\frac{1}{2}}$ vs log [L] gave the one sloping linearity for all systems (see Figure

Table 4.16 A Effects of L-isoleucine concentrations on the polarographic characteristics of Pb (II) -L-isoleucine system,
$[HL]$ = L-isoleucine concentration and
$[L]$ = L-isoleucinate anion concentration

$[HL] \times 10^2$ (M)	pH	$-\log[L]$	$-E_{1/2}$ (V vs SCE)	$E_{1/2}$ (V)	i_d (μA)	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$ (V)
0.00	6.43	-	0.495	-	1.70	0.029
2.00	6.47	4.469	0.497	0.002	1.57	0.030
3.00	6.46	4.303	0.502	0.007	1.54	0.030
4.00	6.48	4.158	0.506	0.011	1.52	0.029
5.00	6.45	4.091	0.508	0.013	1.49	0.029
6.00	6.46	4.002	0.511	0.016	1.48	0.030
7.00	6.47	3.925	0.513	0.018	1.47	0.031
8.00	6.45	3.887	0.514	0.019	1.46	0.031

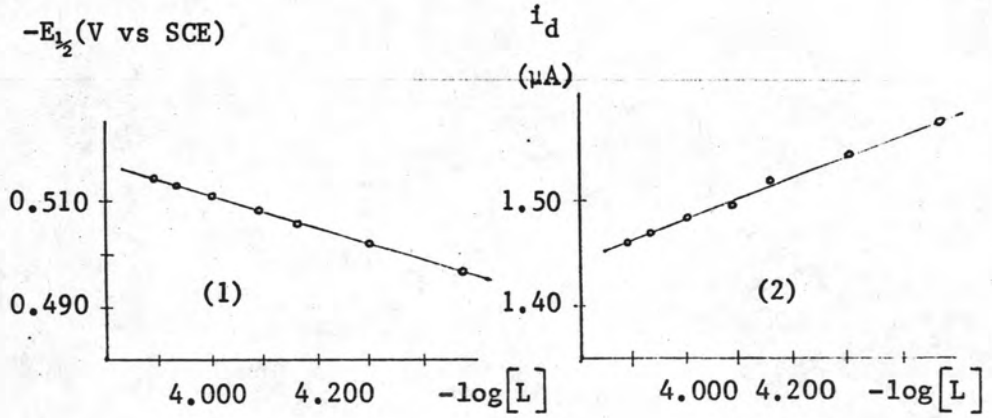

Figure 4.18 A Dependences of L-isoleucinate anion concentrations on $E_{1/2}$ (1) and i_d (2) of Pb(II) -L-isoleucine system

Table 4.16 B Effects of L-leucine concentrations on the polarographic characteristics of Pb (II)-L- leucine system,
[HL] = L-leucine concentration
[L] = L-leucinate anion concentration

$[HL] \times 10^2$ (M)	pH	$-\log[L]$	$-E_{1/2}$ (V vs SCE)	$E_{1/2}$ (V)	i_d (μA)	$E_{3/4} - E_{1/4}$ (V)
0.00	6.43	-	0.495	-	1.70	0.029
2.00	6.52	4.439	0.504	0.009	1.49	0.031
3.00	6.54	4.243	0.510	0.015	1.46	0.030
4.00	6.51	4.148	0.513	0.018	1.43	0.032
5.00	6.49	4.071	0.515	0.020	1.42	0.032
6.00	6.54	3.942	0.519	0.024	1.39	0.030
7.00	6.56	3.855	0.521	0.026	1.38	0.031
8.00	6.47	3.887	0.521	0.026	1.38	0.031

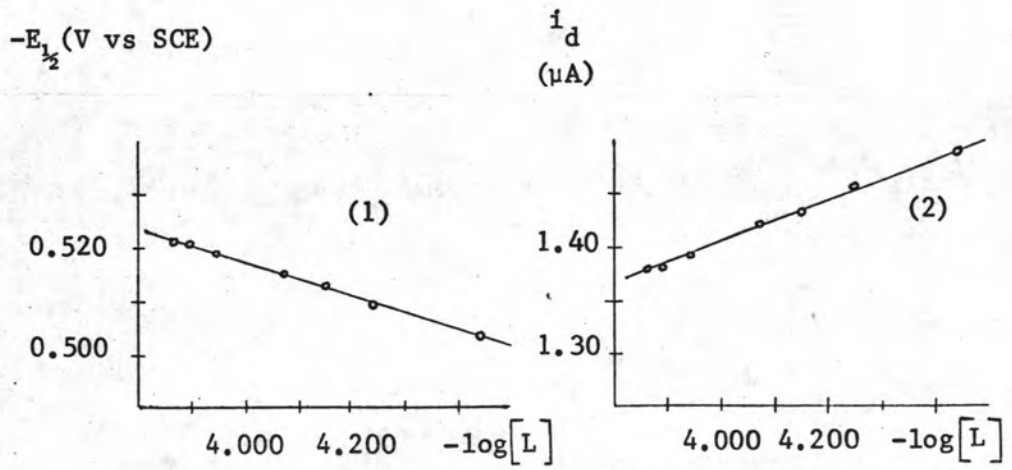

Figure 4.18 B Dependences of L-leucinate anion concentrations on $E_{1/2}$ (1) and i_d (2) of Pb (II) -L-leucine system

Table 4.16 C Effects of L-lysine concentrations on the polarographic characteristics of Pb(II) -L-lysine system,
[HL] = L-lysine concentration and
[L] = L-lysinate anion concentration

$[HL] \times 10^2$ (M)	pH	$-\log[L]$	$-E_{1/2}$ (V vs SCE)	$E_{1/2}$ (V)	i_d (μA)	$E_{3/4} - E_{1/4}$ (V)
0.00	5.53	-	0.495	-	1.80	0.029
2.00	5.55	4.789	0.497	0.002	1.78	0.029
3.00	5.54	4.623	0.496	0.001	1.76	0.029
4.00	5.55	4.488	0.497	0.002	1.74	0.029
5.00	5.53	4.411	0.498	0.003	1.72	0.030
6.00	5.54	4.322	0.496	0.001	1.71	0.030
7.00	5.53	4.265	0.498	0.003	1.70	0.031
8.00	5.52	4.217	0.497	0.002	1.68	0.031

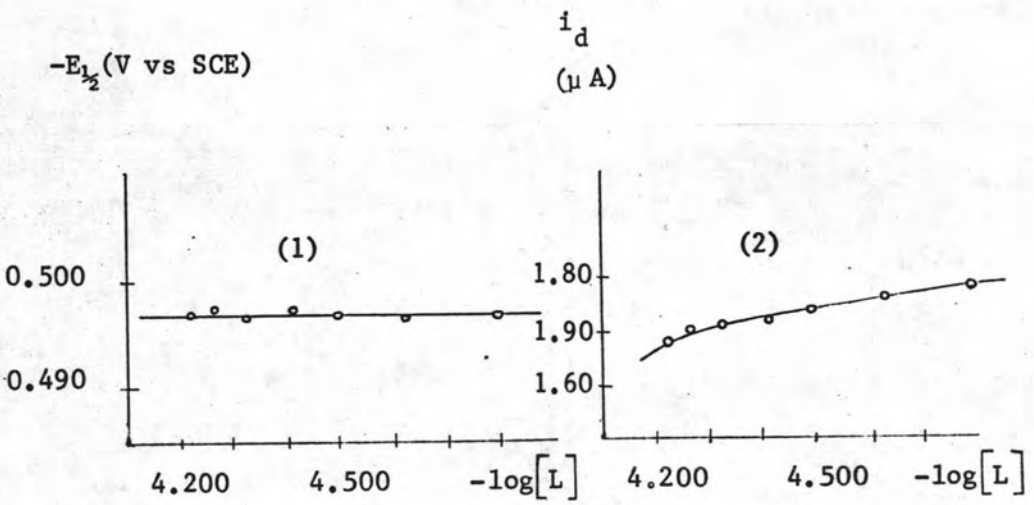

Figure 4.18 C Dependences of L-lysinate anion concentrations on $E_{1/2}$ (1) and i_d (2) of Pb (II) -L-lysine system

Table 4.16 D Effects of L-methionine concentrations on the polarographic characteristics of Pb(II) -L-methionine system, [HL] = L-methionine concentration and [L] = L-methionate anion concentration

$[HL] \times 10^2$ (M)	pH	$-\log[L]$	$-E_{1/2}$ (V vs SCE)	$E_{1/2}$ (V)	i_d (μA)	$E_{3/4} - E_{1/4}$ (V)
0.00	6.53	-	0.495	-	1.70	0.029
2.00	6.55	3.909	0.513	0.018	1.47	0.030
3.00	6.55	3.733	0.518	0.023	1.45	0.029
4.00	6.49	3.668	0.520	0.025	1.42	0.029
5.00	6.48	3.581	0.522	0.027	1.40	0.030
6.00	6.45	3.532	0.524	0.029	1.37	0.031
7.00	6.50	3.415	0.527	0.032	1.33	0.031
8.00	6.57	3.287	0.530	0.035	1.31	0.031

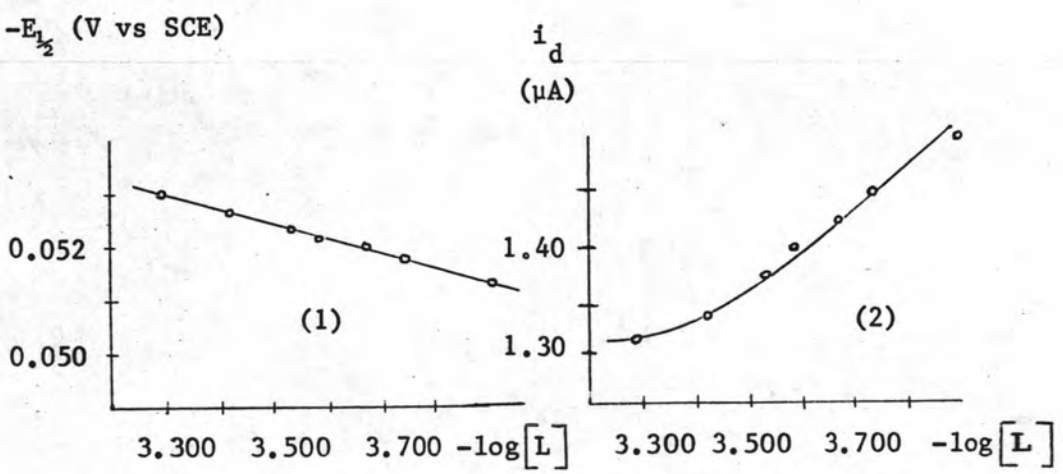

Figure 4.18 D Dependences of L-methionate anion concentrations on $E_{1/2}$(1) and i_d (2) of Pb (II) -L-methionine system

Table 4.16 E Effects of L-phenylalanine concentrations on the polarographic characteristics of Pb(II)-L-phenylalanine system,

$[HL]$ = L-phenylalanine concentration and
$[L]$ = L-phenylalanate anion concentration

$[HL]\times10^2$ (M)	pH	$-\log[L]$	$-E_{1/2}$ (V vs SCE)	$E_{1/2}$ (V)	i_d (μA)	$E_{3/4} - E_{1/4}$ (V)
0.00	7.43	-	0.495	-	1.70	0.029
2.00	7.44	3.109	0.543	0.048	1.43	0.031
3.80	7.49	2.883	0.549	0.054	1.41	0.031
4.00	7.42	2.828	0.551	0.056	1.40	0.030
5.00	7.44	2.711	0.554	0.059	1.39	0.030
6.00	7.43	2.642	0.556	0.061	1.38	0.031
7.00	7.44	2.565	0.558	0.063	1.35	0.031
8.00	7.46	2.487	0.560	0.065	1.31	0.031

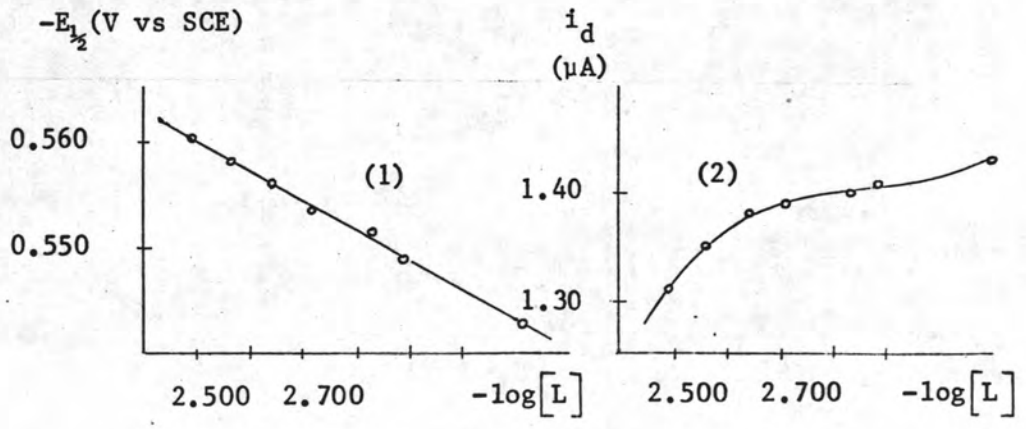

Figure 4.18 E Dependences of L-phenylalanate anion concentration on $E_{1/2}$ (1) and i_d (2) of Pb(II) -L-phenylalanine system

Table 4.16 F Effects of L-threonine concentrations on the polarographic characteristics of Pb (II) -L-threonine system,
$[HL]$ = L-threonine concentration and
$[L]$ = L-threonate anion concentration

$[HL] \times 10^2$ (M)	pH	$-\log[L]$	$-E_{1/2}$ (V vs SCE)	$E_{1/2}$ (V)	i_d (μA)	$E_{3/4} - E_{1/4}$ (V)
0.00	5.43	-	0.495	-	1.70	0.029
2.00	5.48	4.889	0.496	0.001	1.42	0.030
3.00	5.46	4.733	0.500	0.005	1.41	0.030
4.00	5.45	4.618	0.503	0.008	1.40	0.029
5.00	5.46	4.511	0.506	0.011	1.38	0.029
6.00	5.47	4.422	0.509	0.014	1.35	0.031
7.00	5.48	4.345	0.511	0.016	1.33	0.031
8.00	5.45	4.317	0.511	0.016	1.32	0.031

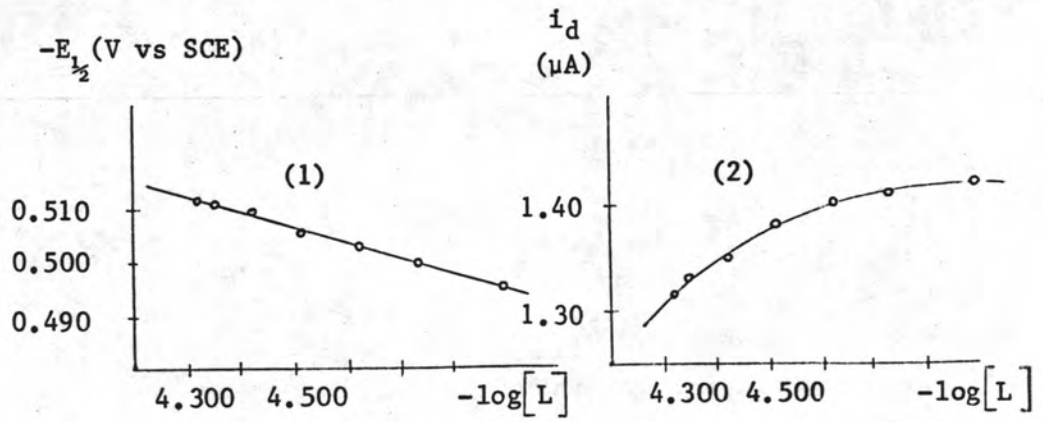

Figure 4.18 F Dependences of L-threonate anion concentrations on $E_{1/2}$ (1) and i_d (2) of Pb(II) -L-threonine system

Table 4.16G Effects of L-tryptophan concentrations on the polarographic characteristics of Pb(II) -L-tryptophan system,

$[HL]$ = L-tryptophan concentration and

$[L]$ = L-tryptophanate anion concentration

$[HL] \times 10^2$ (M)	pH	$-\log[L]$	$-E_{1/2}$ (V vs SCE)	$\Delta E_{1/2}$ (V)	i_d (μA)	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$ (V)
0.00	6.73	-	0.495	-	1.70	0.029
1.00	6.75	4.450	0.520	0.025	1.15	0.030
2.00	6.75	4.149	0.529	0.034	1.12	0.029
3.00	6.74	3.983	0.534	0.039	1.09	0.030
4.00	6.76	3.838	0.538	0.043	1.08	0.030
5.00	6.73	3.771	0.540	0.045	1.06	0.031

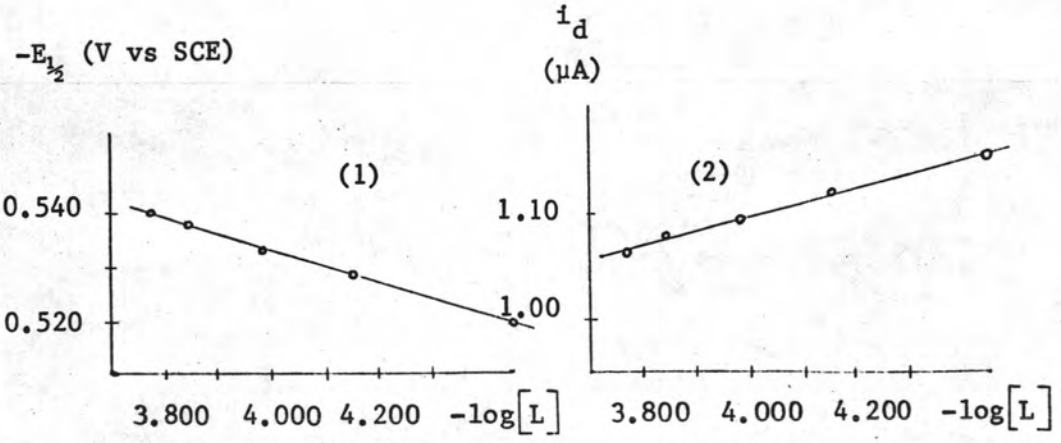

Figure 4.18 G Dependences of L-tryptophante anion concentrations on $E_{1/2}$ (1) and i_d (2) of Pb (II) -L-tryptophan system

Table 4.16 H Effects of L-valine concentrations on the polarographic characteristics of Pb(II) -L-valine system, [HL] = L-valine concentration and [L] = L-valinate anion concentration

$[HL]\times10^2$ (M)	pH	$-\log[L]$	$-E_{1/2}$ (V vs SCE)	$\Delta E_{1/2}$ (V)	i_d (μA)	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$ (V)
0.00	6.53	-	0.495	-	1.98	0.029
2.00	6.55	4.289	0.506	0.011	1.98	0.030
3.00	6.52	4.143	0.510	0.015	1.95	0.030
4.00	6.53	4.008	0.514	0.019	1.92	0.030
5.00	6.52	3.921	0.517	0.022	1.90	0.031
6.00	6.53	3.832	0.519	0.024	1.87	0.031
7.00	6.51	3.785	0.521	0.026	1.85	0.031
8.00	6.54	3.697	0.523	0.028	1.84	0.031

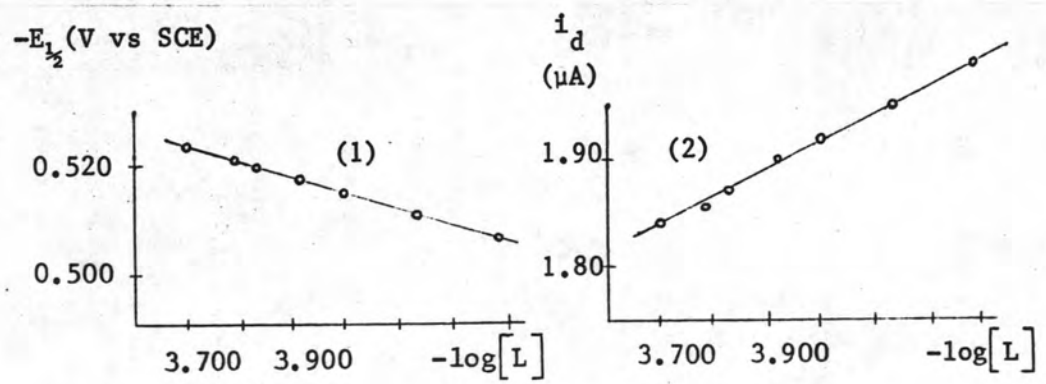

Figure 4.18 H Dependences of L-valinate anion concentrations on $E_{1/2}$ (1) and i_d (2) of Pb (II) -L-valine system

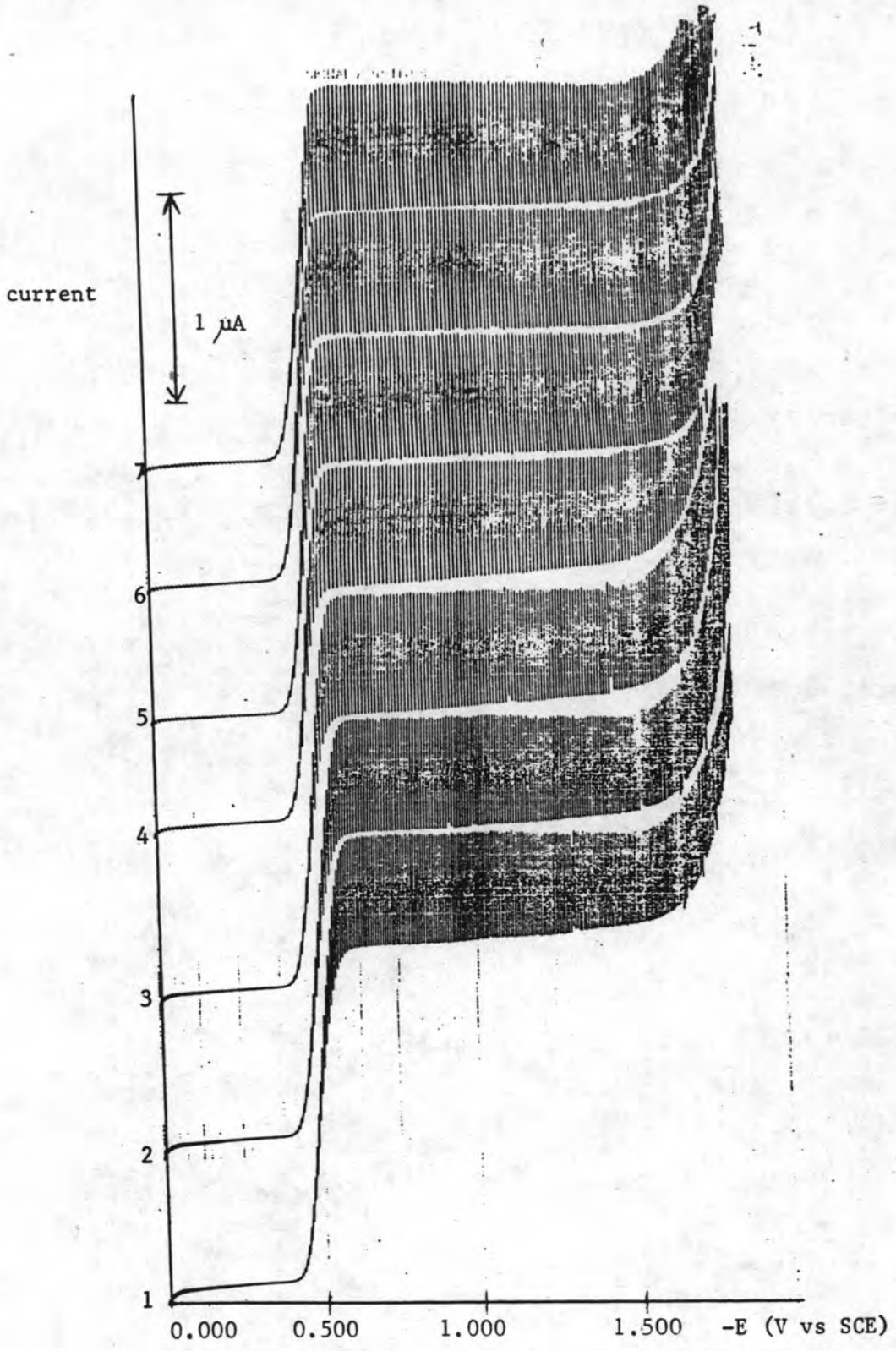

Figure 4.17 A Polarograms of 1.00×10^{-4} M Pb (II) ion and various concentrations of L-isoleucine in borate buffer and 0.10 M KCl ; 1) 8.00×10^{-2} M pH 6.45, 2) 7.00×10^{-2} M pH 6.47, 3) 6.00×10^{-2} M pH 6.46, 4) 5.00×10^{-2} M pH 6.45, 5) 4.00×10^{-2} M pH 6.48, 6) 3.00×10^{-2} M pH 6.46 and 7) 2.00×10^{-2} M pH 6.47

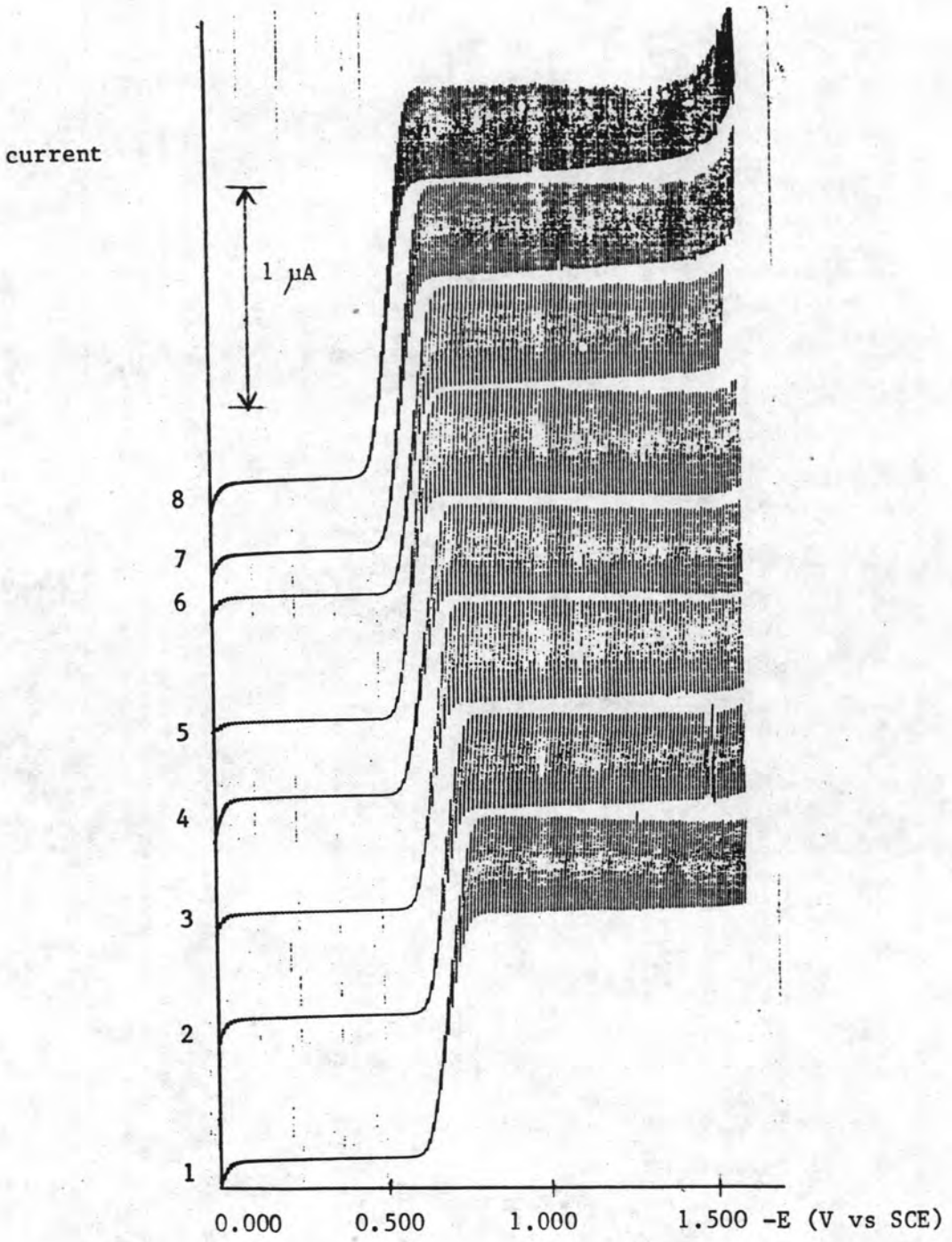

Figure 4.17 B Polarograms of 1.00×10^{-4} M Pb(II) ion and various concentrations of L-threonine in borate buffer and 0.10 M KCl ; 1) 8.00×10^{-2} M pH 5.45, 2) 7.00×10^{-2} M pH 5.48, 3) 6.00×10^{-2} M pH 5.47, 4) 5.00×10^{-2} M pH 8.46, 5) 4.00×10^{-2} M pH 5.45, 6) 3.00×10^{-2} M pH 5.46, 7) 2.00×10^{-2} M pH 5.48 and 8) 0.00 M pH 5.43

Table 4.17 A Effect of h on i_d of Pb(II) -L-isoleucine system

h(cm)	$h^{\frac{1}{2}}(cm^{\frac{1}{2}})$	$i_d(\mu A)$
40.0	6.32	1.47
50.0	7.07	1.76
60.0	7.75	1.95
70.0	8.37	2.00

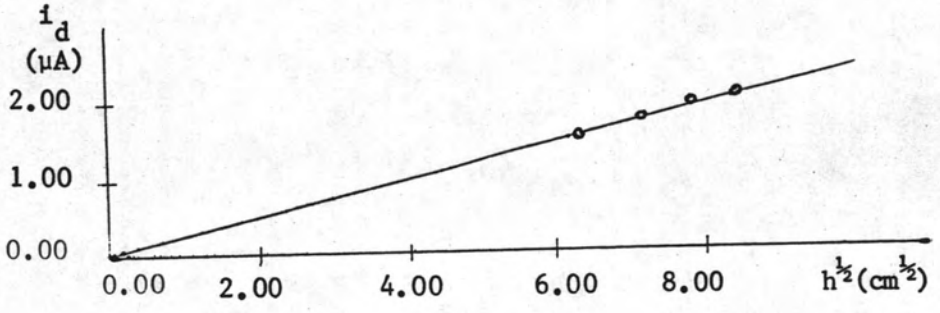

Figure 4.19 A Dependence of $h^{\frac{1}{2}}$ on i_d of Pb(II) -L-isoleucine system

Table 4.17 B Effect of h on i_d of Pb(II) -L-leucine system

h(cm)	$h^{1/2}(cm^{1/2})$	$i_d(\mu A)$
40.0	6.32	1.38
50.0	7.07	1.65
60.0	7.75	1.88
70.0	8.37	1.90

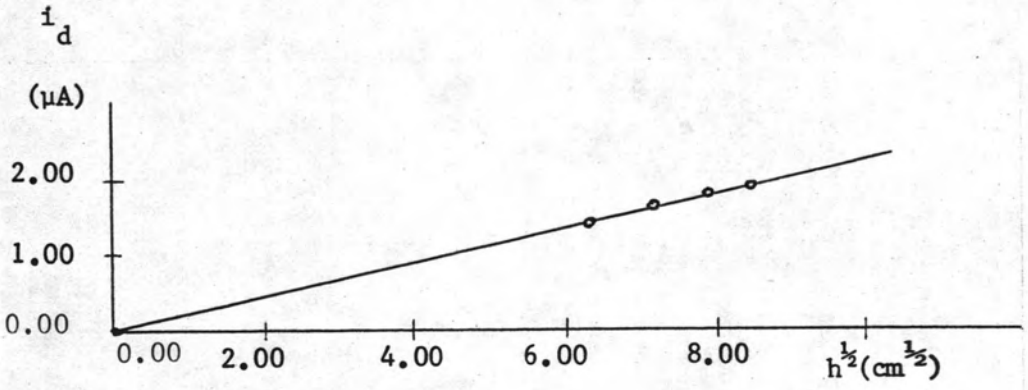

Figure 4.19 B Dependence of $h^{1/2}$ on i_d of Pb(II) -L-leucine system

Table 4.17 C Effect of h on i_d of Pb(II) -L-lysine system

h(cm)	$h^{\frac{1}{2}}(cm^{\frac{1}{2}})$	$i_d(\mu A)$
40.0	6.32	1.72
50.0	7.07	2.10
60.0	7.75	2.33
70.0	8.37	2.38

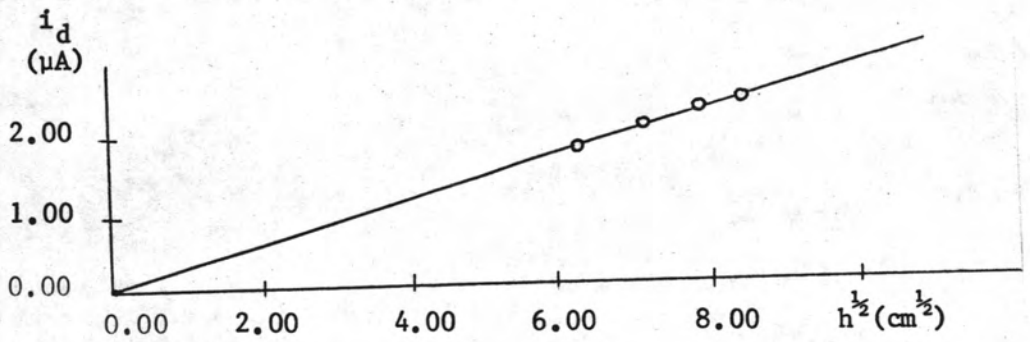

Figure 4.19 C Dependence of $h^{\frac{1}{2}}$ on i_d of Pb(II) -L-lysine system

Table 4.17 D Effect of h on i_d of Pb(II) -L-methionine system

h(cm)	$h^{\frac{1}{2}}(cm^{\frac{1}{2}})$	$i_d(\mu A)$
40.0	6.32	1.31
50.0	7.07	1.46
60.0	7.75	1.62
70.0	8.37	1.85

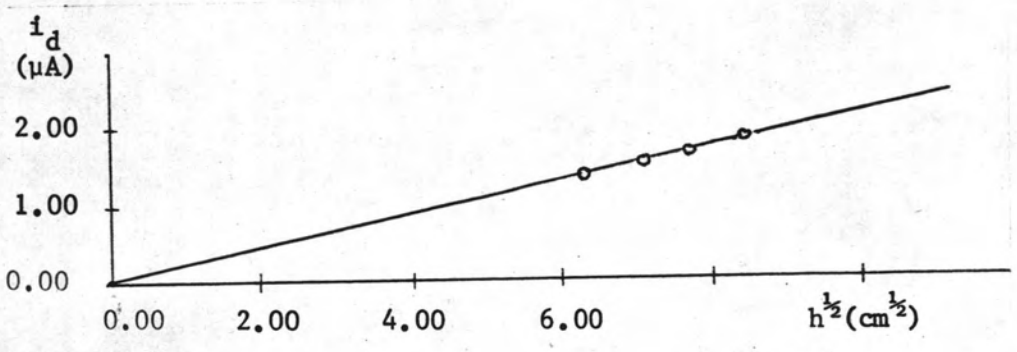

Figure 4.19 D Dependence of $h^{\frac{1}{2}}$ on i_d of Pb(II) -L-methionine system

Table 4.17 E Effect of h on i_d of Pb(II) -L-phenylalanine system

h(cm)	$h^{\frac{1}{2}}(cm^{\frac{1}{2}})$	$i_d(\mu A)$
40.0	6.32	1.38
50.0	7.07	1.51
60.0	7.75	1.63
70.0	8.37	1.75

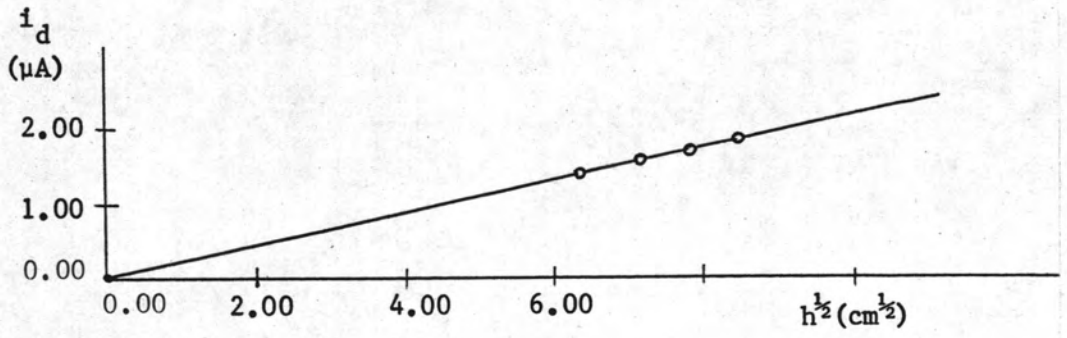

Figure 4.19 E Dependence of $h^{\frac{1}{2}}$ on i_d of Pb(II) -L-phenylalanine system

Table 4.17 F Effect of h on i_d of Pb(II) -L-threonine system

h(cm)	$h^{\frac{1}{2}}(cm^{\frac{1}{2}})$	$i_d(\mu A)$
40.0	6.32	1.42
50.0	7.07	1.80
60.0	7.75	2.03
70.0	8.37	2.11

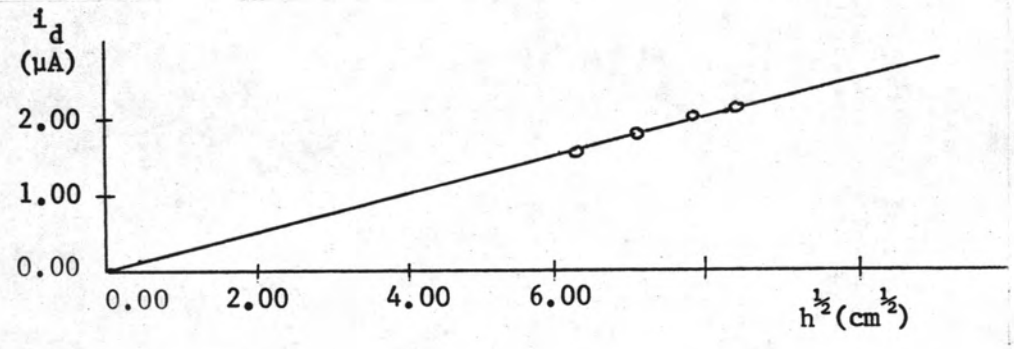

Figure 4.19 F Dependence of $h^{\frac{1}{2}}$ on i_d of Pb(II) -L-threonine system

Table 4.17 G Effect of h on i_d of Pb(II) -L-tryptophan system

h(cm)	$h^{1/2}(cm^{1/2})$	$i_d(\mu A)$
40.0	6.32	1.12
50.0	7.07	1.31
60.0	7.75	1.42
70.0	8.37	1.50

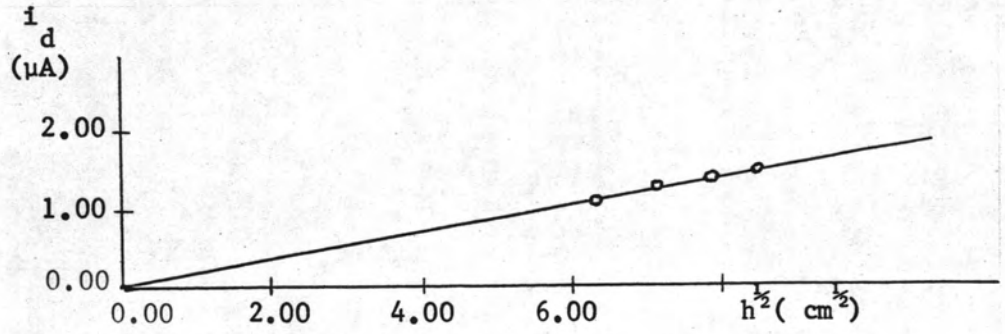

Figure 4.19 G Dependence of $h^{1/2}$ on i_d of Pb(II) -L-tryptophan system

Table 4.17 H Effect of h on i_d of Pb(II) -L-valine system

h(cm)	$h^{\frac{1}{2}}(cm^{\frac{1}{2}})$	$i_d(\mu A)$
40.0	6.32	1.92
50.0	7.07	2.20
60.0	7.75	2.32
70.0	8.37	2.51

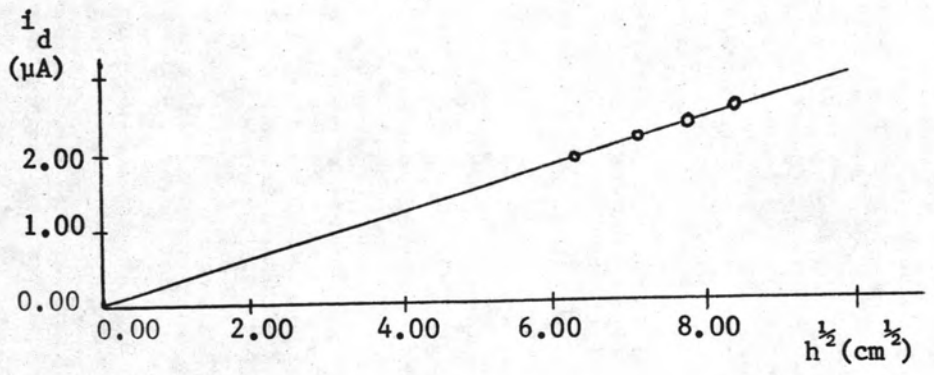

Figure 4.19 H Dependence of $h^{\frac{1}{2}}$ on i_d of Pb(II) -L-valine system

4.18 A - 4.18 H), excepted of Pb(II)-L-lysine system gave the linearity paralleled to the x-axis (see Figure 4.18 C) thereby the single complex was formed for all systems excepted for Pb(II)-L-lysine system. In order to confirm these results, the plots of $\Delta E_{\frac{1}{2}}$ vs log [L] by least squares analysis were performed and they also showed one sloping linear portion for each system (see Figure 4.20 A - 4.20 H) excepted for Pb(II)-L-lysine system that showed non-sloping linear portion (see Figure 4.20 C). The value of j corresponding to the value of log β_j of the complexes was worked out from the slope and the intercept of the plots of $\Delta E_{\frac{1}{2}}$ vs log [L], respectively, by equation (2.22) and as in the preceding section. In case of the Pb(II)-L-lysine system, the value of the slope was zero which resulted in the zero value of j by equation (2.22). In case of those systems other than the Pb(II)-L-lysine system, the values of the linear correlation coefficient (γ), the slope and the intercept of each linear portion from the plots of $\Delta E_{\frac{1}{2}}$ vs log [L] (Figure 4.20 A - 4.20 H) including the corresponding values of j and log β_j were collected as shown in Table 4.18. From Table 4.18, the values of j became 1 ($j \approx 1$), therefore it could be said that the composition of the Pb(II) ion to L-isoleucine, Pb(II) ion to L-leucine, Pb(II) ion to L-methionine, Pb(II) ion to L-phenylalanine, Pb(II) ion to L-threonine, Pb(II) ion to L-tryptophan and Pb(II) ion to L-valine was 1:1 in each case and no evidences of complex formation in the solutions of Pb(II)-L-lysine system by the polarographic analysis.

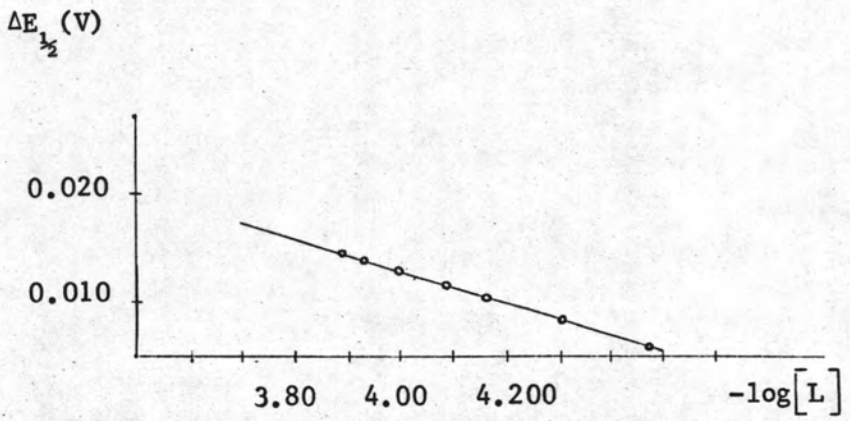

Figure 4.20 A Dependence of L-isoleucinate anion concentrations on $\Delta E_{1/2}$ of Pb(II)-L-isoleucine system

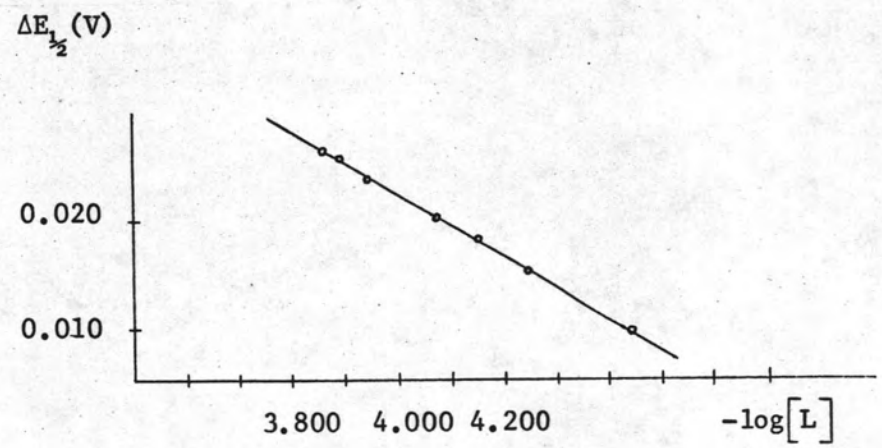

Figure 4.20 B Dependence of L-leucinate anion concentrations on $\Delta E_{1/2}$ of Pb(II) -L-leucine system

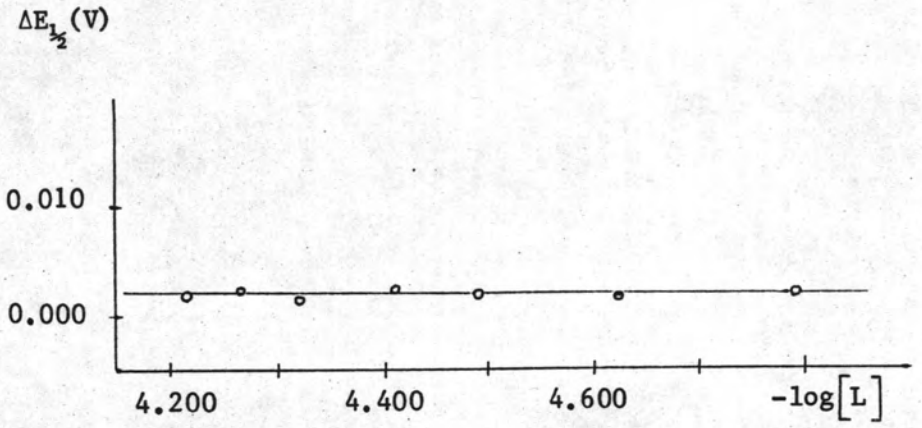

Figure 4.20 C Dependence of L-lysinate anion concentrations on $\Delta E_{\frac{1}{2}}$ of Pb(II) -L-lysine system

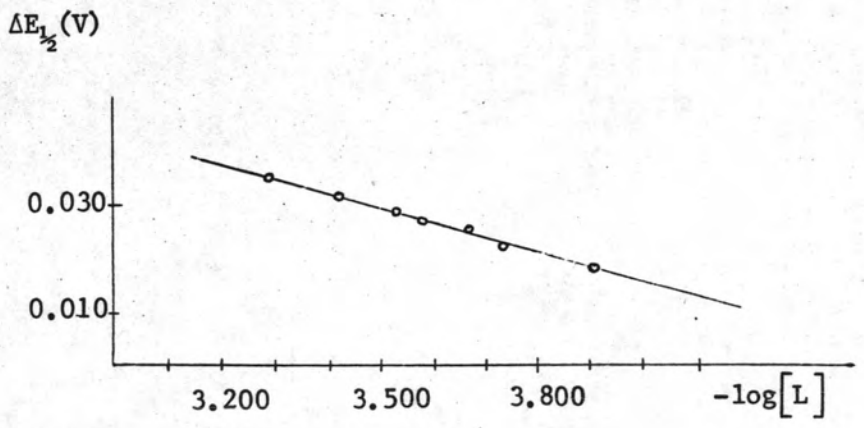

Figure 4.20 D Dependence of L-methionate anion concentrations on $\Delta E_{\frac{1}{2}}$ og Pb(II) -L-methionine system

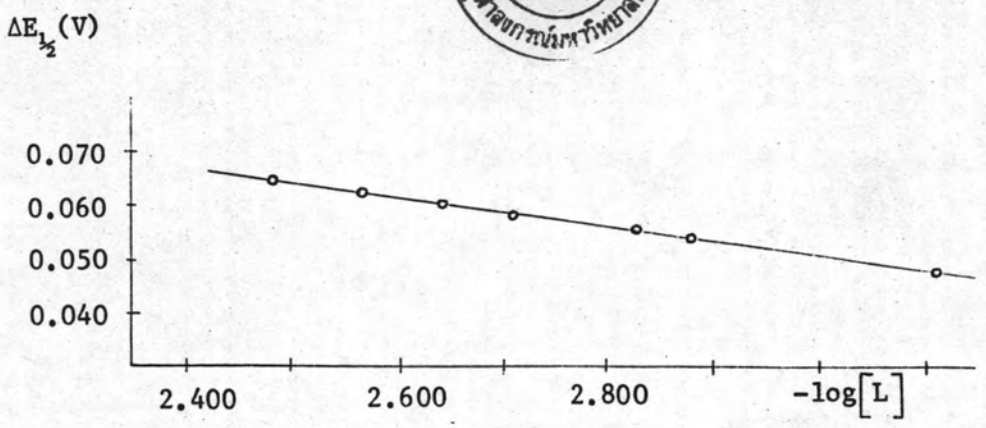

Figure 4.20 E Dependence of L-phenylalanate anion concentrations on $\Delta E_{1/2}$ of Pb(II) -L-phenylalanine system

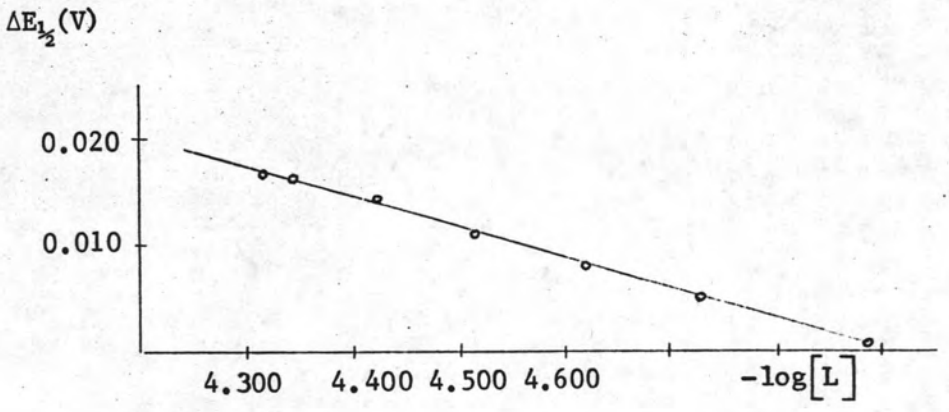

Figure 4.20 F Dependence of L-threonate anion concentrations on $\Delta E_{1/2}$ of Pb(II) -L-threonine system

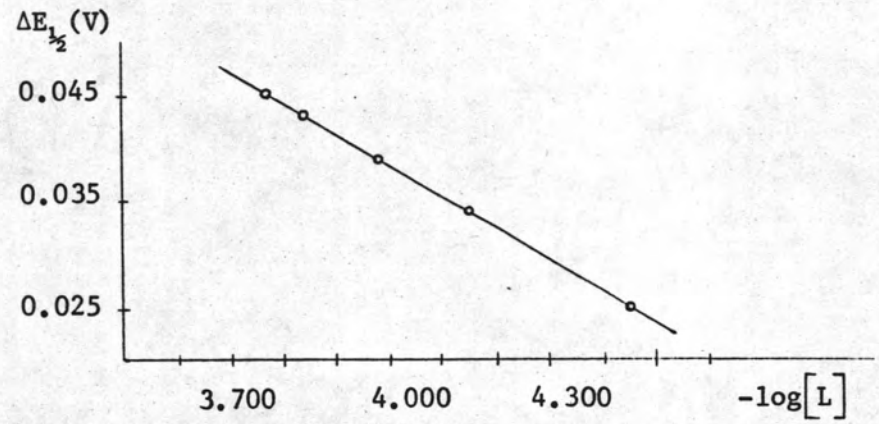

Figure 4.20 G Dependence of L-tryptophanate anion concentrations on $\Delta E_{\frac{1}{2}}$ of Pb(II) -L-tryptophan system

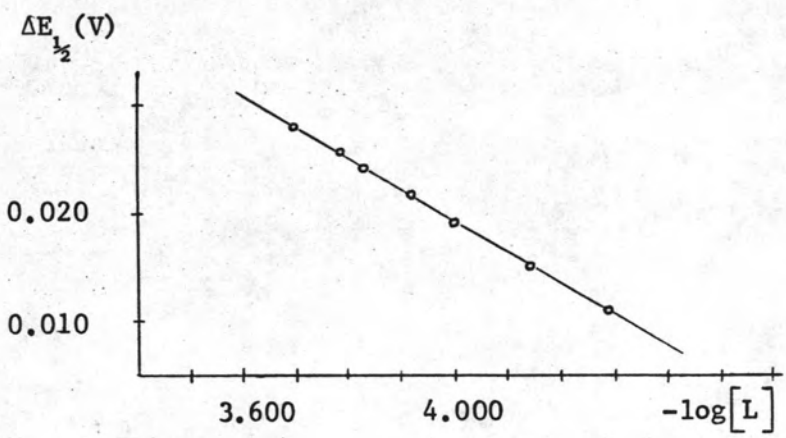

Figure 4.20 H Dependence of L-valinate anion concentrations on $\Delta E_{\frac{1}{2}}$ of Pb(II) -L-valine system

Table 4.18 Obtained values from the linear plot of $\Delta E_{\frac{1}{2}}$ vs log [L] from Pb(II)-essential amino acid complexes by polarographic technique

anion of Pb complex	linear correlation coefficient(γ)	slope	j	inter-cept	log β_j	Remarks
L-isoleucine	0.999	0.029	0.94	0.133	4.33	
L-leucine	0.998	0.030	0.98	0.141	4.59	
L-lysine	-	-	-	-	-	no evidence of complex formation
L-methionine	0.998	0.028	0.91	0.126	4.10	
L-phenylalanine	0.999	0.028	0.91	0.134	4.36	
L-threonine	0.998	0.027	0.88	0.134	4.36	
L-tryptophan	0.999	0.029	0.94	0.156	5.07	
L-valine	0.999	0.029	0.94	0.136	4.42	